Effect of Ionizing Radiation on a Series of Saturated Polyesters

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SUMMARY

The effect of ionizing radiation on a series of saturated linear polyesters containing the repeating unit $-\!\!\left[\,OC-R_1-COO-R_2-O\,\right]_n$, in which R_1 and R_2 are linear or branched alkylene groups, is reported. Cross-linking and scission were shown to be influenced greatly by the structural features of R_1 and R_2 and the intrinsic viscosities of the polymers. A dose-rate independence was observed for the polymers in vacuo, whereas in air, degradation was related to diffusion of the gas into the polymer. Amorphous polymers were shown to cross-link more readily than the crystalline and oriented polyesters; trapped radicals in the crystalline polymers cause delayed cross-linking when the polymers were subsequently heated.

A fundamental difference was found for the grafting of monovinyl and multivinyl monomers to the polyesters. Multivinyl monomers were much more efficient than monovinyl monomers in producing cross-links and caused cross-linking in polyesters which normally degrade on irradiation alone or in the presence of monovinyl monomers. The term "bridge grafting" is proposed for this effect of the multivinyl monomers; bridge grafting can be applied to a large number of polymers to (1) reduce the irradiation dosage in those polymers

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which cross-link readily, and (2) cross-link readily those polymers which cross-link with difficulty, or not at all, because of high scission degradation.

INTRODUCTION

When a polymer is subjected to ionizing radiation, either a cross-linked or degraded polymer is obtained. In the past few years, the influence of such radiation on many polymers has been reported and reviewed in detail [1, 2], and numerous attempts have been made to correlate the cross-linking or the degradation of the polymer to molecular weight [1], to the monomer and polymer structures [3-5], to the effect of oxygen [6, 7], to the protection of aryl groups [8], to the linkages present in the polymer [5, 9], and to other factors (pp. 49-60 of [1]).

To date the literature in the field of polymer irradiation has dealt predominantly with the available addition polymers of commercial importance, even though there are many important condensation polymers. The number of condensation polymers studied has been limited. The most important classes of condensation polymers were not considered to undergo any notable improvement in properties under the influence of ionizing radiation (p. 173 of [1]). The phenolic resins [10], as well as the melamine-formaldehyde and urea-formaldehyde resins [10] and polysulfide elastomers [11-13], are easily degraded by ionizing radiation. The polyamides [3, 9, 10] and the polyurethanes [10] are cross-linked by irradiation with a decrease in some of their physical properties. Polyethylene terephthalate has received the most attention [3, 10, 14-16] and appears to be more resistant to radiation than many other polymers. As a class of condensation polymers, the unsaturated polyesters have also been studied (see [11]). Charlesby and co-workers studied radiation reactions of unsaturated polyesters and also reported [17] that one saturated linear polyester did not change in solubility or viscosity after irradiation. These results are in marked contrast to the effects produced on unsaturated analogous structures, all of which cross-linked, and differ from the effects of radiation on addition polymers containing ester groups. The acrylate polymers, in which the ester groups are located in the side chains, belong to this latter class and are known to be cross-linked by ionizing radiation [11, 17, 18].

There is no published detailed study on the effect of ionizing radiation on simple carboxylic esters, and the influence of side-chain ester groups in the acrylates cannot be considered as applicable directly to polymers having ester links in the backbone chain, as in the saturated linear polyesters. However, it may be concluded

from a comparison of the polyacrylates [18] and polyethylene [19] that the ester group can act as an energy sink in stabilizing the polymer chain against scission as well as cross-linking.

Also, there have been no detailed publications on the effect of irradiation on the saturated polyesters or on related condensation polymers such as the polyamides of amino acids. This information would be invaluable in human welfare because living cells are composed primarily of proteins and nucleic acids. Little is known about how radiation reacts with protein polymers to produce mutation effects or cause destruction of tissue. The state of knowledge on polymer irradiation is still too meager to apply the results to such complicated polymers as proteins, but as the research is extended from simple to more complicated molecules, it may be possible eventually to understand the behavior of the proteins. Compared with the polymers found in living entities, the polyesters are relatively simple polymers, and, for this reason, among others, a series of saturated linear polyesters was prepared and subjected to ionizing radiation.

The polymers used in this study are the polyesters of dihydric alcohols, $HO-R_1-OH$, and dicarboxylic acids, $HOOC-R_2-COOH$; they have in their structures as the repeating unit $-OC-R_1-COO-R_2-O-$. As a class, these polyesters are well known and readily prepared. The information derived from these studies could be extended readily to the polyesters derived from hydroxycarboxylic acids, which are not as well known and have the repeating unit $-O-R_1-CO-$ in their structures. An obvious extension of this class of polyesters, $-O-R_1-CO-$, are the polyamides of ω-amino acids $\left(\text{which have the repeating unit } -\overset{\displaystyle R}{\underset{\displaystyle |}{N}}-R_1-CO- \right)$.

The proteins, $\left(\overset{\displaystyle R}{\underset{\displaystyle |}{N}}-CR_2CO \right)_n$, are the first members of the latter series. The knowledge gained in studies of such polymers should be useful also in the "molecular engineering" [20] of polymers for specific applications in space and other environments where ionizing radiation is prevalent, and in synthesizing polymers with specific cross-linking characteristics.

The saturated polyesters were chosen for this study because they could be readily prepared autocatalytically to any desired molecular weight. This characteristic afforded a means of correlating radiation effects with the molecular weights of the polymer. The fact that the polyesters could be prepared autocatalytically eliminates the possibility of catalyst contamination, which could lead to misinterpretation of the effects of irradiation.

Since the pendant ester group has been shown to be an energy

sink [18], it was desirable to investigate the effect of radiation on polymers which contain the ester group as an integral part of the polymer backbone. To determine the effect of this type of structure, it was necessary to consider polymer systems which could be prepared with a predetermined structure in the main chain. In polyesters, the structure of the polymer can be varied by the proper choice of the starting diol or the diacid, or both; thus a convenient method for changing the nature of the $-R_1-$ and $-R_2-$ structures in the chain is afforded. If $-R_1-$ and $-R_2-$ are methylene, $-CH_2-$, groups, the ratio of the number of methylene groups to the number of carboxyl groups in the acid, or to the number of hydroxyl groups in the diol, or to the number of ester groups in the polymer, can be varied at will. The effect of this variable has not yet been reported in the literature. In branched vinyl addition polymers, such as in polyethylene, an exact correlation of the br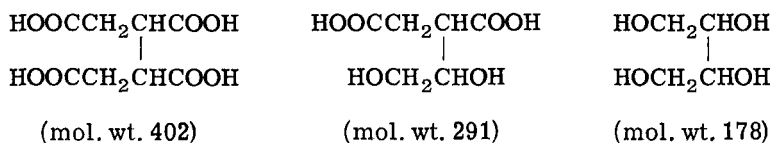anched structure with the cross-linking efficiency of irradiation is difficult to assess because of the random nature of the branching. In attempts to overcome this problem by copolymerizing a branch containing monomer, such as propylene, with a nonbranched monomer, such as ethylene, the same difficulties of interpretation would be encountered, because of the random combination of the monomers. However, polyesterification also affords a means of preparing a series of polymers of predetermined ordered branches along the chain by the proper selection of branched dicarboxylic acids or branched dils (e.g., methyl- and ethyl-substituted diacids or diols). Also, the branch can be selected to act as a known energy sink as in the case where it is an aromatic ring [8]. In using this approach, an appropriate series of polyesters of various molecular weights was synthesized and subjected to ionizing radiation. The changes in the polymers were observed by noting changes in the intrinsic viscosity, after first determining if the presence of oxygen influenced the results obtained. The effects of different radiation sources and dose-rate dependency were also studied. The studies were extended to the grafting monovinyl and divinyl monomers to determine their influence in modifying the cross-linking reaction.

The use of condensation polyesters offers other potential advantages over vinyl addition polymers with regard to chemical analysis of the irradiated polymers. It should be possible to hydrolyze the polyesters, and any new bonds formed by irradiation, if they are carbon to carbon bonds, would not be destroyed by the hydrolysis. The new molecules, which would be admixed with the regenerated initial diols and diacids, could then be identified or otherwise characterized. This property is in contrast to that of vinyl addition polymers whose main chain contains only carbon to carbon linkages. Since in most cases the new bonds formed on irradiating vinyl polymers are carbon to carbon bonds and the ruptures are random carbon to carbon scissions, a diagnostic degradation appears to be futile.

With the polyesters, three new types of molecules could result from the formation of a new bond between two chains: a tetracarboxylic acid (A), a dihydroxy dicarboxylic acid (B), and a tetrahydric alcohol (C):

$$
\begin{array}{ccc}
\text{HOOC—R}_1\text{—COOH} & \text{HOOC—R}_2\text{—COOH} & \text{HO—R}_2\text{—OH} \\
| & | & | \\
\text{HOOC—R}_1\text{—COOH} & \text{HO—R}_2\text{—OH} & \text{HO—R}_2\text{—OH} \\
\\
\text{(A)} & \text{(B)} & \text{(C)}
\end{array}
$$
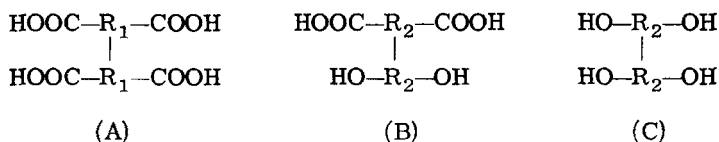
It becomes apparent that as the number of carbon atoms in the R_1 and R_2 groups increases, the number of possible isomers increases and complicates the characterization of the product. Irradiated polyethylene succinate would be an ideal polymer to subject to diagnostic saponification because only three compounds, neglecting optical isomers, are possible:

$$
\begin{array}{ccc}
\text{HOOCCH}_2\text{CHCOOH} & \text{HOOCCH}_2\text{CHCOOH} & \text{HOCH}_2\text{CHOH} \\
| & | & | \\
\text{HOOCCH}_2\text{CHCOOH} & \text{HOCH}_2\text{CHOH} & \text{HOCH}_2\text{CHOH} \\
\\
\text{(mol. wt. 402)} & \text{(mol. wt. 291)} & \text{(mol. wt. 178)}
\end{array}
$$

Unfortunately, it was found that polyethylene succinate does not cross-link upon irradiation, and, for that reason, polytetramethylene sebacate was selected for a preliminary study.

EXPERIMENTAL

Reagents and Polyester Syntheses

The reagents used in the present studies and their sources are given in Table 1. The diacid and the diol in a 1 : 1.05 mole ratio were condensed by using a modification of Carothers procedure [21, 22]. Nitrogen was used as an inert atmosphere to prevent peroxide formation and other oxidation products. The polycondensations were performed initially at atmospheric pressure and, in the more advanced stages, at reduced pressures of 0.1 to 0.5 mm Hg at temperatures in the range 200-250°C until the desired viscosity range was obtained. In this manner, the related polymers of approximately the same composition and of at least two different molecular weights were prepared. In most cases, four polymers of varying molecular weights were isolated. The polyesters that were prepared are given in Tables 2 and 3. The conditions under which the individual polymers of various initial intrinsic viscosity

Table 1. Reagents and Their Sources

Reagents[a]	Source
Succinic acid	Eastman Organic Chemicals Co.
Glutaric acid	Eastman Organic Chemicals Co.
Adipic acid	E. I. du Pont de Nemours & Co.
Sebacic acid	Harchem. Div. of Wallace & Tiernan, Inc.
3, 3-Dimethyl glutaric acid	Aldrich Chemical Co.
3-Methyl adipic acid	Aldrich Chemical Co.
Azelaic acid	Aldrich Chemical Co.
Methyl succinic acid	b
2, 3-Diphenyl succinic acid	c
Ethylene glycol	Fisher Scientific Co.
Propanediol-1, 3	Eastman Organic Chemicals Co.
Butanediol-1, 4	Antara Chemicals Div. of General Aniline and Film Co.
Pentanediol-1, 5	Carbide and Carbon Chemical Co.
Propanediol-1, 2	Dow Chemical Co.
2, 3-Dimethyl propanediol-1, 3	Eastman Chemical Products, Inc.
2, 2-Diethyl propanediol-1, 3	Carbide and Carbon Chemical Co.
3-Methyl pentanediol-1, 5	Carbide and Carbon Chemical Co.
Chloroform	Fisher reagent grade
Nitrogen[d]	Cleveland Wire Div. of General Electric Co.
Styrene[e]	Foster Grant Co.
Divinylbenzene[f]	Dow Chemical Co.
Dowex 50 and Dowex 2 resins	Dow Chemical Co.

[a]All commercial-grade chemicals were purified before use either by fractional distillation or crystallization, and the purity of the compounds was verified by checking melting points or refractive indices.

[b]Itaconic acid supplied by Chas. Pfizer & Co. was hydrogenated with W-6 Raney nickel at 25°C.

[c]2, 3-Diphenyl succinyl nitrile was hydrolyzed with 96% H_2SO_4 supplied by R. B. Davis, C.S.C., Dept. Chemistry, Univ. Notre Dame.

[d]99. 99+% purity; oxygen content less than 5 ppm.

[e]99. 83% purity.

[f]50. 2% divinylbenzenes; 49. 8% ethyl styrenes.

Table 2. Straight-Chain Polyesters Investigated

Polymer	Carbon atoms in:	
	Alcohol	Acid
Poly(ethylene succinate)	2	4
Poly(ethylene adipate)	2	6
Poly(ethylene azelate)	2	9
Poly(ethylene sebacate)	2	10
Poly(trimethylene succinate)	3	4
Poly(trimethylene adipate)	3	6
Poly(trimethylene sebacate)	3	10
Poly(tetramethylene succinate)	4	4
Poly(tetramethylene adipate)	4	6
Poly(tetramethylene sebacate)	4	10
Poly(pentamethylene succinate)	5	4
Poly(pentamethylene adipate)	5	6
Poly(pentamethylene azelate)	5	9
Poly(pentamethylene sebacate)	5	10
Poly(decamethylene sebacate)	10	10

before irradiation were prepared are given in the footnotes in Tables 4 to 38. Table 2 gives the unsubstituted straight-chain polyesters, and Table 3 gives their alkyl- and aryl-substituted polyesters, which, for the purposes of this paper, are considered as having branches which may influence the effects due to ionizing radiation.

Irradiation of Polyesters

The irradiation of the polyesters was performed in most cases with use of the ARCO Mark I microwave linear accelerator at the Applied Radiation Corporation, Walnut Creek, California, and at the ARCO Midwest Radiation facilities in Rockford, Illinois. This accelerator operates at a beam energy of 8 MeV and can completely penetrate 4 cm of unit-density material. The molten polymer samples were cast into 1.5-cm glass vials in a deoxygenated nitrogen atmosphere and sealed in this condition. The beam width was

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Table 3. Branched-Chain Polyesters Investigated

| | Carbon atoms in: | | | |
| | Alcohol | | Acid | |
Polymer	Main chain[a]	Branch	Main chain[a]	Branch
Poly(1-methylethylene succinate)	2	1 × 1	4	
Poly(1-methylethylene adipate)	2	1 × 1	6	
Poly(1-methylethylene azelate)	2	1 × 1	9	
Poly(1-methylethylene sebacate)	2	1 × 1	10	
Poly(2,2-dimethyltrimethylene succinate)	3	2 × 1	4	
Poly(2,2-dimethyltrimethylene adipate)	3	2 × 1	6	
Poly(2,2-dimethyltrimethylene azelate)	3	2 × 1	9	
Poly(2,2-dimethyltrimethylene sebacate)	3	2 × 1	10	
Poly(2,2-diethyltrimethylene succinate)	3	2 × 2	4	
Poly(2,2-diethyltrimethylene adipate)	3	2 × 2	6	
Poly(2,2-diethyltrimethylene azelate)	3	2 × 2	9	
Poly(2,2-diethyltrimethylene sebacate)	3	2 × 2	10	
Poly(3-methylpentamethylene succinate)	5	1 × 1	4	
Poly(3-methylpentamethylene adipate)	5	1 × 1	6	
Poly(3-methylpentamethylene azelate)	5	1 × 1	9	
Poly(3-methylpentamethylene sebacate)	5	1 × 1	10	
Poly(2,2-dimethyltrimethylene-3,3-dimethyl glutarate)	3	2 × 1	5	2 × 1
Poly(3-methylpentamethylene-3-methyl adipate)	5	1 × 1	6	1 × 1
Poly(pentamethylene-2,3-diphenyl succinate)	5		4	2 × 6
Poly(pentamethylene-2-methyl succinate)	5		4	1 × 1

[a]Number of carbon atoms in main chain.
[b]Number of carbon atoms in branch; the expression 2 × 1 signifies that there are two branches each of which contains one carbon atom, and 2 × 6 signifies two branches each of which contains six carbon atoms.

about 10 cm; the average beam power during irradiation was 530 w with 180 pulses/sec, with a pulse length of 6 μsec, and with a peak current of 50 mA. The sample vials were placed on a turntable of 13 ft in circumference, which rotated at 7 rpm under a vertically mounted wave guide. Air from cooling blowers was directed at the sample vials to maintain the temperature of the samples at about 50°C. Since, at the dose rate obtained in this accelerator, heat is generated within the sample, those polymers which melt below 50°C softened or melted. During periodic inspection of the sample vials,

gas bubbles were noted in some of the molten polymers as a result of the evolution of gaseous irradiation byproducts. Dosimetry was based on the change in the optical density of cobalt glass, which had been standardized against the primary standard of calorimetry [23]. To determine the effect of dose rate and the influence of the nature of the source of ionizing radiation, some of the polymers were irradiated by using a 2-MeV van de Graaff electron accelerator of the Radiation Laboratory, University of Notre Dame, at 25, 50, and 100 μA and an underground 1200-C cobalt-60 source [24].

Intrinsic Viscosities

Freshly distilled chloroform was used. as the solvent for measuring the intrinsic viscosities. The polymer concentrations were 0. 8, 0. 4, and 0. 2 g per 100 ml, and the intrinsic viscosities $[\eta]$ were calculated from the relationship $[\eta] = \lim_{c \to 0} (\eta_{sp}/C)$ [see 25]. The measurements of the intrinsic viscosities were made with an Ubbelohde viscometer in a constant-temperature bath at $25 \pm 0.05°C$.

Correlation of Intrinsic Viscosity with Absorbed Radiation Dose

The effects of ionizing radiation on the intrinsic viscosity of the respective polymers are summarized in Tables 4 to 38 and graphically presented in Figs. 1 to 35. The term gel, which appears in both the tables and figures, refers to those polyesters which have been converted from linear soluable polymers to three-dimensional polymers which were insoluble in boiling chloroform as a result of cross-linking.

Effect of Dose Rate and Source of Ionizing Radiation on Intrinsic Viscosity

Three films of polytetramethylene sebacate having thicknesses of 10 mm were introduced in glass tubes, and the tubes were then evacuated for 24 hr by means of a mercury diffusion pump to a pressure of 1×10^{-6} mm Hg, sealed, and subjected to irradiation by the cobalt-60 source, the van de Graaff, and the ARCO linear accelerator to a total dose of 6 megareps. The dose rate varied from 1 mrep/hr for the cobalt-60 in the location in which the sample was placed to dose rates of about 1400 mrep/min in the ARCO accelerator during the pulses of actual irradiation in the sample. The data on the changes in the intrinsic viscosity of the polymer are given in Table 39 and shown graphically in Fig. 36.
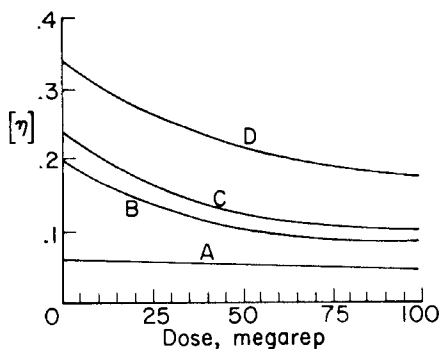
Fig. 1. Effect of irradiation on intrinsic viscosity of poly(ethylene succinate) $+(CH_2)_2-OCO-(CH_2)_2-OCO+_n$. See Table 4.

Table 4. Effect of Irradiation on Intrinsic Viscosity of Poly(ethylene succinate) (See Fig. 1)

Dose, Mrep	Intrinsic viscosity, $[\eta]$			
	A	B	C	D
0	0.060[a]	0.190[b]	0.238[c]	0.312[d]
5	0.059	0.182	0.206	0.341
10	0.059	0.160	0.172	0.324
25	0.059	0.116	0.143	0.260
50	0.059	0.101	0.112	0.232
100	0.048	0.086	0.090	0.168

[a]At 250°C for 6 hr at 1 atm.
[b]At 235°C for 5 hr at 1 atm, then for 5 hr at 0.3 mm.
[c]At 250°C for 5 hr at 1 atm, then for 10 hr at 0.5 mm.
[d]At 250°C for 6 hr at 1 atm, then for 20 hr at 0.5 mm.
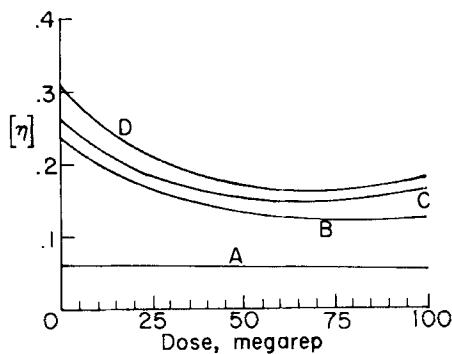
Fig. 2. Effect of irradiation on intrinsic viscosity of poly(ethylene adipate) $+(CH_2)_2=OCO-(CH_2)_4-OCO+_n$. See Table 5.

Table 5. Effect of Irradiation on Intrinsic Viscosity of Poly(ethylene adipate) (See Fig. 2)

Dose, Mrep	Intrinsic viscosity, $[\eta]$			
	A	B	C	D
0	0.050[a]	0.248[b]	0.274[c]	0.326[d]
5	0.056	0.193	0.248	0.247
10	0.050	0.197	0.183	0.257
25	0.068	0.178	0.214	0.205
50	0.058	0.148	0.148	0.156
100	0.060	0.130	0.187	0.203

[a]At 250°C for 6 hr at 1 atm.
[b]At 250°C for 6 hr at 1 atm, then for 5 hr at 0.1 mm.
[c]At 250°C for 5 hr at 1 atm, then for 10 hr at 0.1 mm.
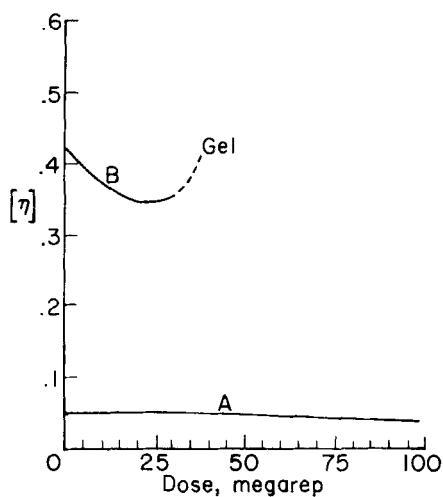[d]At 250°C for 6 hr at 1 atm, then for 20 hr at 0.3 mm.

Fig. 3. Effect of irradiation on intrinsic viscosity of poly(ethylene azelate) $+(CH_2)_2-OCO-(CH_2)_7-OCO+_n$. See Table 6.

Table 6. Effect of Irradiation on Intrinsic Viscosity of Poly(ethylene azelate) (See Fig. 3)

Dose, Mrep	Intrinsic viscosity, $[\eta]$	
	A	B
0	0.068[a]	0.404[b]
5	0.054	0.418
10	0.053	0.354
25	0.039	0.336
50	0.041	Gel
100	0.040	Gel

[a]At 250°C for 6 hr at 1 atm.
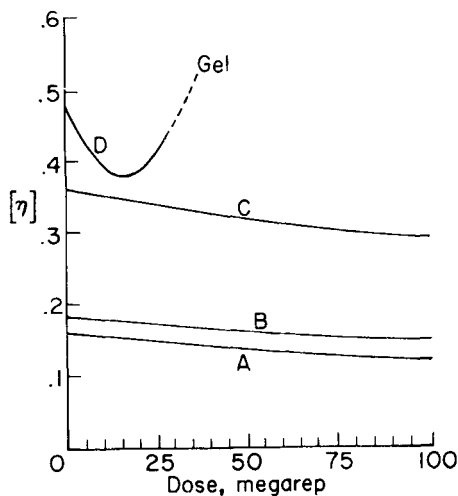[b]At 250°C for 6 hr at 1 atm, then for 10 hr at 0.5 mm.

Fig. 4. Effect of irradiation on intrinsic viscosity of poly(ethylene sebacate) $+(CH_2)_2-OCO-(CH_2)_8-OCO]_n$. See Table 7.

Table 7. Effect of Irradiation on Intrinsic Viscosity of Poly(ethylene sebacate) (See Fig. 4)

Dose Mrep	Intrinsic viscosity, $[\eta]$			
	A	B	C	D
0	0.161[a]	0.178[b]	0.369[c]	0.464[d]
5	0.160	0.170	0.355	0.465
10	0.162	0.171	0.350	0.365
25	0.150	0.157	0.347	0.421
50	0.142	0.148	0.323	Gel
100	0.136	0.150	0.274	Gel

[a]At 250°C for 6 hr at 1 atm.
[b]At 250°C for 6 hr at 1 atm, then for 5 hr at 0.5 mm.
[c]At 250°C for 6 hr at 1 atm, then for 10 hr at 0.7 mm.
[d]At 250°C for 6 hr at 1 atm, then for 20 hr at 0.5 mm.
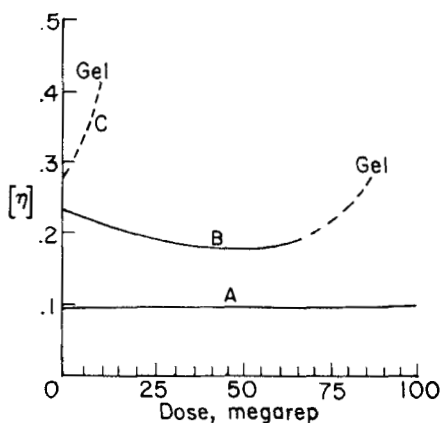
Fig. 5. Effect of irradiation on intrinsic viscosity of poly(trimethylene succinate) $+(CH_2)_3—OCO—(CH_2)_2—OCO+_n$. See Table 8.

Table 8. Effect of Irradiation on Intrinsic Viscosity of Poly(trimethylene succinate) (See Fig. 5)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.090[a]	0.236[b]	0.280[c]
5	0.094	0.221	Gel
10	0.094	0.206	Gel
25	0.094	0.180	Gel
50	0.094	0.164	Gel
100	0.094	Gel	Gel

[a]At 250°C for 6 hr at 1 atm.
[b]At 250°C for 5 hr at 1 atm, then for 10 hr at 0.1 mm.
[c]At 255°C for 6 hr at 1 atm, then for 20 hr at 0.7 mm.
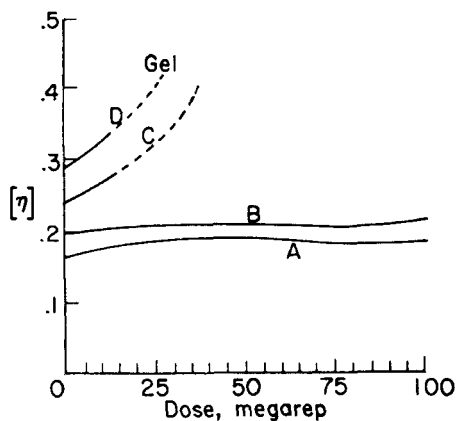
Fig. 6. Effect of irradiation on intrinsic viscosity of poly(tri-
methylene adipate) $\{(CH_2)_3\text{—}OCO\text{—}(CH_2)_4\text{—}OCO\}_n$. See Table 9.

Table 9. Effect of Irradiation on Intrinsic Viscosity of Poly(tri-
methylene adipate) (See Fig. 6)

Dose, Mrep	Intrinsic viscosity, $[\eta]$			
	A	B	C	D
0	0.152[a]	0.200[b]	0.251[c]	0.291[d]
5	0.174	0.200	0.263	0.320
10	0.190	0.197	0.275	0.330
25	0.196	0.196	Gel	Gel
50	0.202	0.187	Gel	Gel
100	0.197	0.228	Gel	Gel

[a]At 250°C for 6 hr at 1 atm.
[b]At 250°C for 6 hr at 1 atm, then for 5 hr at 0.2 mm.
[c]At 250°C for 6 hr at 1 atm, then for 10 hr at 1.5 mm.
[d]At 250°C for 6 hr at 1 atm, then for 20 hr at 1.0 mm.
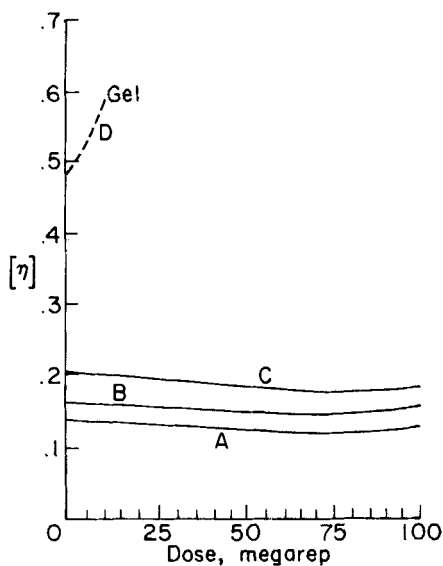
Fig. 7.   Effect of irradiation on intrinsic viscosity of poly(tri-methylene sebacate) $+(CH_2)_3$—OCO—$(CH_2)_8$—OCO$\frac{1}{n}$. See Table 10.

Table 10.   Effect of Irradiation on Intrinsic Viscosity of Poly(tri-methylene sebacate) (See Fig. 7)

| Dose, Mrep | Intrinsic viscosity, $[\eta]$ | | | |
	A	B	C	D
0	0.145[a]	0.148[b]	0.207[c]	0.496[d]
5	0.138	0.148	0.196	Gel
10	0.136	0.142	0.196	Gel
25	0.136	0.140	0.200	Gel
50	0.136	0.149	0.188	Gel
100	0.134	0.148	0.180	Gel

[a] At 250°C for 6 hr at 1 atm.
[b] At 240°C for 5 hr at 1 atm, then for 5 hr at 0.1 mm.
[c] At 240°C for 5 hr at 1 atm, then for 10 hr at 0.1 mm.
[d] At 250°C for 6 hr at 1 atm, then for 20 hr at 0.1 mm.

Fig. 8. Effect of irradiation on intrinsic viscosity of poly(tetra-methylene succinate) $+(CH_2)_4-OCO-(CH_2)_2-OCO+_n$. See Table 11.

Table 11. Effect of Irradiation on Intrinsic Viscosity of Poly(tetra-methylene succinate) (See Fig. 8)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.153[a]	0.239[b]	0.378[c]
5	0.164	Gel	0.590
10	0.151	Gel	0.630
25	0.150	Gel	Gel
50	0.143	Gel	Gel
100	0.122	Gel	Gel

[a]At 255°C for 5.5 hr at 1 atm.
[b]At 240°C for 4 hr at 1 atm, then for 10 hr at 0.5 mm.
[c]At 230°C for 4 hr at 1 atm, then for 20 hr at 0.1 mm.
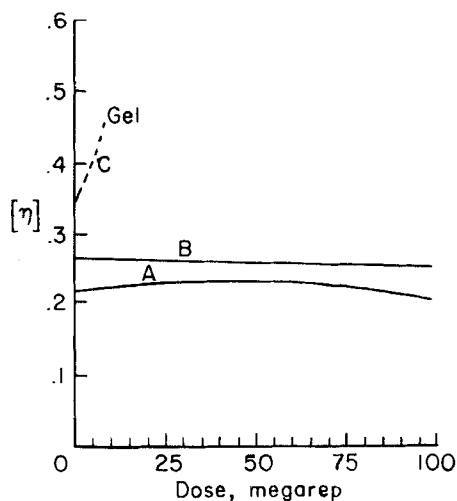
Fig. 9. Effect of irradiation on intrinsic viscosity of poly(tetra-methylene adipate) $+(CH_2)_4-OCO-(CH_2)_4-OCO\frac{1}{n}$. See Table 12.

Table 12. Effect of Irradiation on Intrinsic Viscosity of Poly(tetra-methylene adipate) (See Fig. 9)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.202[a]	0.262[b]	0.343[c]
5	0.210	0.259	Gel
10	0.215	0.259	Gel
25	0.204	0.252	Gel
50	0.210	0.235	Gel
100	0.202	0.242	Gel

[a]At 250°C for 5 hr at 1 atm.
[b]At 260°C for 5 hr at 1 atm, then for 10 hr at 0.1 mm.
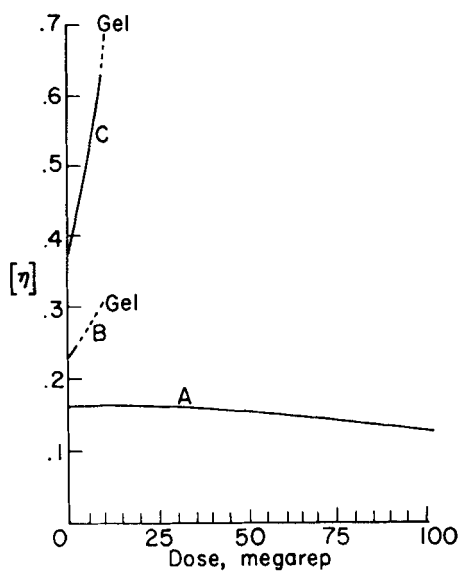[c]At 225°C for 5 hr at 1 atm, then for 20 hr at 0.4 mm.
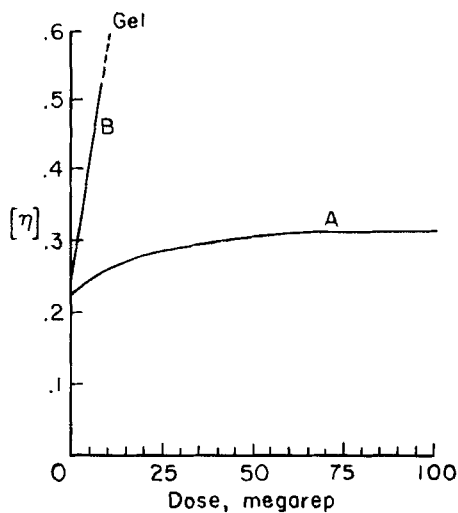
Fig. 10. Effect of irradiation on intrinsic viscosity of poly(tetra-methylene sebacate) $+(CH_2)_4-OCO-(CH_2)_8-OCO\frac{}{n}$. See Table 13.

Table 13. Effect of Irradiation on Intrinsic Viscosity of Poly(tetra-methylene sebacate) (See Fig. 10)

Dose, Mrep	Intrinsic viscosity, $[\eta]$	
	A	B
0	0. 230[a]	0. 258[b]
5	0. 248	0. 548
10	0. 274	Gel
25	0. 274	Gel
50	0. 270	Gel
100	0. 282	Gel

[a]At 255°C for 5. 5 hr at 1 atm.
[b]At 255°C for 6 hr at 1 atm, then for 20 hr at 1. 0 mm.

Fig. 11. Effect of irradiation on intrinsic viscosity of poly(penta-methylene succinate) $-(CH_2)_5-OCO-(CH_2)_2-OCO-_n$. See Table 14.

Table 14. Effect of Irradiation on Intrinsic Viscosity of Poly(penta-methylene succinate) (See Fig. 11)

Dose, Mrep	Intrinsic viscosity, $[\eta]$	
	A	B
0	0.186[a]	0.190[b]
5	0.213	0.270
10	0.276	Gel
25	Gel	Gel
50	Gel	Gel
100	Gel	Gel

[a]At 245°C for 6 hr at 1 atm.
[b]At 240°C for 5 hr at 1 atm, then for 20 hr at 0.3 mm.
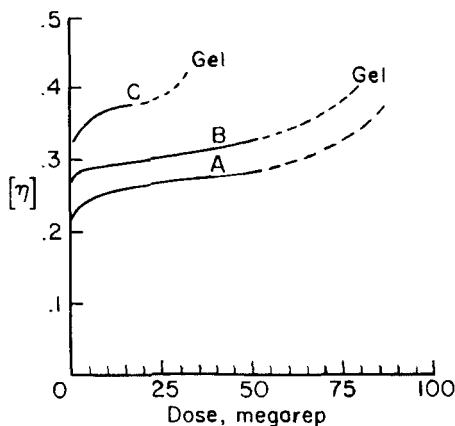
Fig. 12. Effect of irradiation on intrinsic viscosity of poly(penta-methylene adipate) $\{(CH_2)_5-OCO-(CH_2)_4-OCO\}_n$. See Table 15.

Table 15. Effect of Irradiation on Intrinsic Viscosity of Poly(penta-methylene adipate) (See Fig. 12)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.232[a]	0.280[b]	0.338[c]
5	0.264	0.292	0.351
10	0.268	0.290	0.363
25	0.272	0.308	Gel
50	0.274	0.330	Gel
100	Gel	Gel	Gel

[a] At 255°C for 5 hr at 1 atm.
[b] At 250°C for 5 hr at 1 atm, then for 10 hr at 0.2 mm.
[c] At 250°C for 5 hr at 1 atm, then for 15 hr at 0.3 mm.
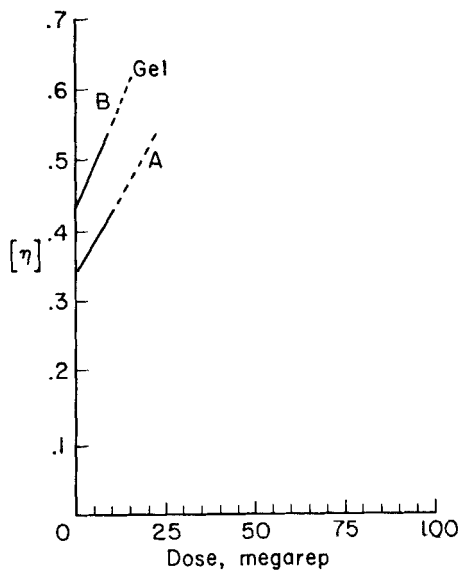
Fig. 13. Effect of irradiation on intrinsic viscosity of poly(penta-methylene azelate) $+(CH_2)_5-OCO-(CH_2)_7-OCO +_n$. See Table 16.

Table 16. Effect of Irradiation on Intrinsic Viscosity of Poly(penta-methylene azelate) (See Fig. 13)

Dose, Mrep	Intrinsic viscosity, $[\eta]$	
	A	B
0	0.350[a]	0.445[b]
5	0.372	0.483
10	0.418	0.534
25	Gel	Gel
50	Gel	Gel
100	Gel	Gel

[a]At 250°C for 6 hr at 1 atm, then for 3 days at 0.2 mm.
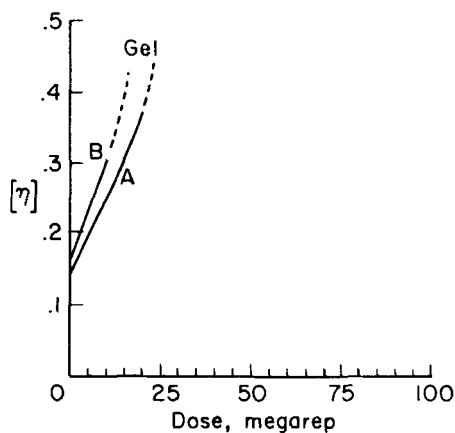[b]At 250°C for 6 hr at 1 atm, then for 4 days at 0.2 mm.
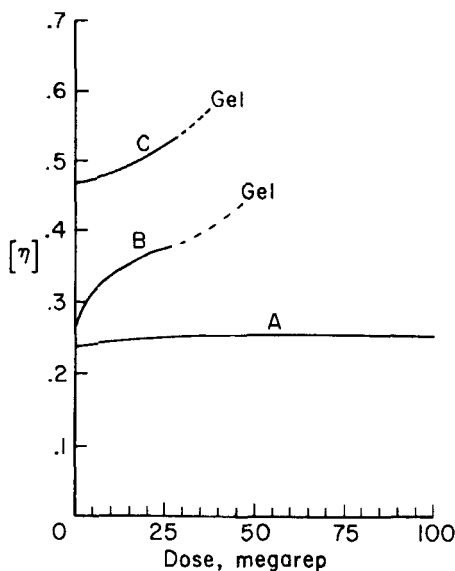
Fig. 14. Effect of irradiation on intrinsic viscosity of poly(penta-methylene sebacate) $\{(CH_2)_5\text{—}OCO\text{—}(CH_2)_8\text{—}OCO\}_n$. See Table 17.

Table 17. Effect of Irradiation on Intrinsic Viscosity of Poly(penta-methylene sebacate) (See Fig. 14)

Dose, Mrep	Intrinsic velocity $[\eta]$		
	A	B	C
0	0.237[a]	0.264[b]	0.480[c]
5	0.222	0.340	0.474
10	0.254	0.340	0.486
25	0.220	0.364	0.518
50	0.242	Gel	Gel
100	0.234	Gel	Gel

[a]At 255°C for 5.5 hr at 1 atm.
[b]At 265°C for 3 hr at 1 atm, then for 9.5 hr at 5 mm.
[c]At 250°C for 6 hr at 1 atm, then for 20 hr at 0.05 mm.
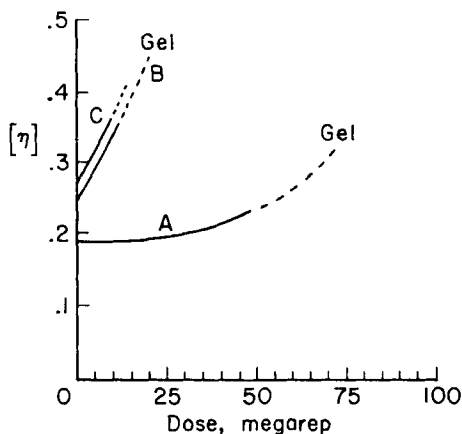
Fig. 15. Effect of irradiation on intrinsic viscosity of poly(deca-methylene sebacate) $+(CH_2)_{10}-OCO-(CH_2)_8-OCO+_n$. See Table 18.

Table 18. Effect of Irradiation on Intrinsic Viscosity of Poly(deca-methylene sebacate) (See Fig. 15)

Dose, Mrep	Intrinsic viscosity $[\eta]$		
	A	B	C
0	0. 189[a]	0. 260[b]	0. 270[c]
5	0. 185	0. 324	0. 326
10	0. 195	0. 360	0. 312
25	0. 213	Gel	Gel
50	0. 205	Gel	Gel
100	Gel	Gel	Gel

[a]At 210°C for 6 hr at 1 atm.
[b]At 210°C for 5 hr at 1 atm, then for 30 hr at 0. 5 mm.
[c]At 210°C for 5 hr at 1 atm, then for 48 hr at 0. 5 mm.
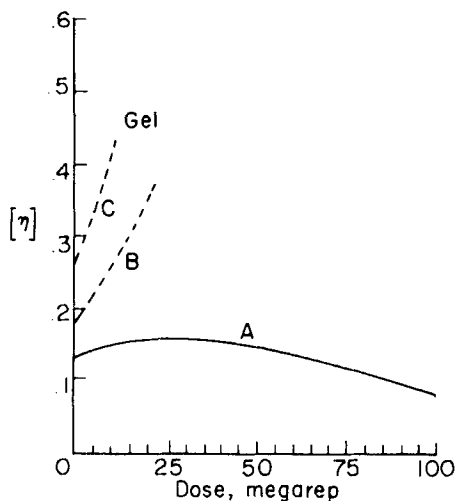
Fig. 16. Effect of irradiation on intrinsic viscosity of poly(1-methylethylene succinate) $+(CH_2-CH(CH_3)-OCO-(CH_2)_2-OCO+_n$. See Table 19.

Table 19. Effect of Irradiation on Intrinsic Viscosity of Poly(1-methylethylene succinate) (See Fig. 16)

Dose, Mrep	Intrinsic viscosity $[\eta]$		
	A	B	C
0	0.108[a]	0.194[b]	0.270[c]
5	0.156	Gel	Gel
10	0.166	Gel	Gel
25	0.129	Gel	Gel
50	0.129	Gel	Gel
100	0.082	Gel	Gel

[a]At 220°C for 6 hr at 1 atm.
[b]At 220°C for 6 hr at 1 atm, then for 2 days at 0.3 mm.
[c]At 220°C for 6 hr at 1 atm, then for 3 days at 0.3 mm.
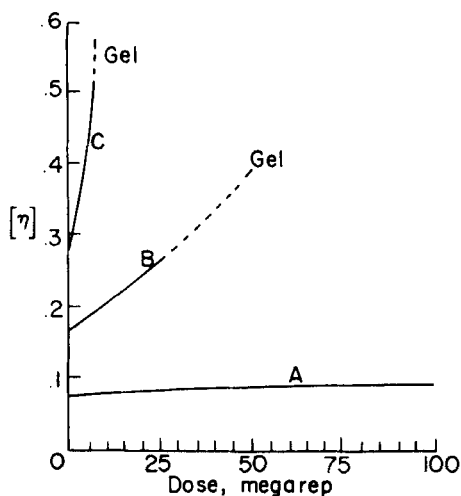
Fig. 17. Effect of irradiation on intrinsic viscosity of poly(1-methylethylene adipate) $+(CH_2-HC(CH_3)-OCO-(CH_2)_4-OCO]_n$. See Table 20.

Table 20. Effect of Irradiation on Intrinsic Viscosity of Poly(1-methylethylene adipate) (See Fig. 17)

Dose, Mrep	Intrinsic viscosity $[\eta]$		
	A	B	C
0	0.082[a]	0.160[b]	0.284[c]
5	0.080	0.188	0.524
10	0.079	0.222	Gel
25	0.068	0.236	Gel
50	0.074	Gel	Gel
100	0.080	Gel	Gel

[a] At 220°C for 6 hr at 1 atm.
[b] At 220°C for 6 hr at 1 atm, then for 1 day at 0.3 mm.
[c] At 220°C for 6 hr at 1 atm, then for 2 days at 0.3 mm.
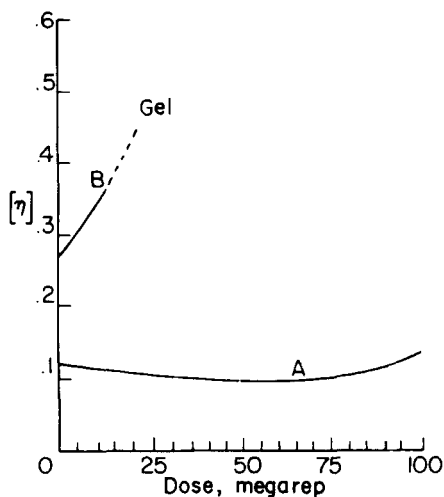
Fig. 18. Effect of irradiation on intrinsic viscosity of poly(1-methylethylene azelate) $\{CH_2-CH(CH_3)-OCO-(CH_2)_7-OCO\}_n$. See Table 21.

Table 21. Effect of Irradiation on Intrinsic Viscosity of Poly(1-methylethylene azelate) (See Fig. 18)

Dose, Mrep	Intrinsic viscosity, $[\eta]$	
	A	B
0	0.112[a]	0.284[b]
5	0.093	0.289
10	0.078	0.314
25	0.090	Gel
50	0.129	Gel
100	0.101	Gel

[a]At 220°C for 6 hr at 1 atm.
[b]At 220°C for 6 hr at 1 atm, then for 1 day at 0.3 mm.
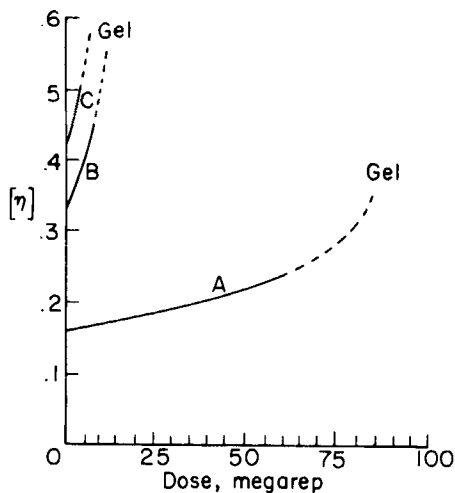
Fig. 19. Effect of irradiation on intrinsic viscosity of poly(1-methylethylene sebacate) $\left[CH_2-CH(CH_3)-OCO-(CH_2)_8-OCO\right]_{\overline{m}}$.
See Table 22.

Table 22. Effect of Irradiation on Intrinsic Viscosity of Poly(1-methylethylene sebacate) (See Fig. 19)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.238[a]	0.338[b]	0.402[c]
5	0.235	0.450	Gel
10	0.247	Gel	Gel
25	0.253	Gel	Gel
50	Gel	Gel	Gel
100	Gel	Gel	Gel

[a]At 220°C for 6 hr at 1 atm.
[b]At 220°C for 6 hr at 1 atm, then for 2 days at 0.3 mm.
[c]At 220°C for 6 hr at 1 atm, then for 3 days at 0.3 mm.
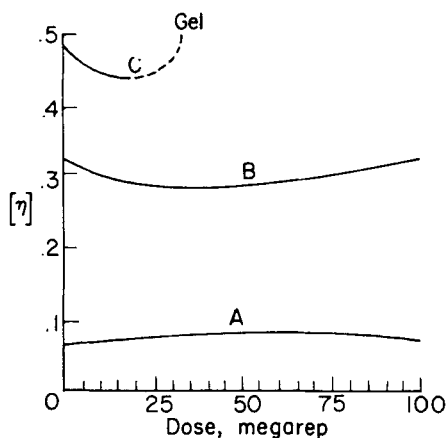
Fig. 20. Effect of irradiation on intrinsic viscosity of poly(2, 2-dimethyltrimethylene succinate) $+CH_2-C(CH_3)_2-CH_2-OCO-(CH_2)_2-OCO]_n$. See Table 23.

Table 23. Effect of Irradiation on Intrinsic Viscosity of Poly(2, 2-dimethyltrimethylene succinate) (See Fig. 20)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0. 050[a]	0. 310[b]	0. 489[c]
5	0. 061	0. 275	0. 451
10	0. 057	0. 281	0. 426
25	0. 054	0. 250	Gel
50	0. 068	0. 270	Gel
100	0. 053	0. 316	Gel

[a]At 220°C for 6 hr at 1 atm.
[b]At 220°C for 6 hr at 1 atm, then for 1 day at 0. 3 mm
[c]At 220°C for 6 hr at 1 atm, then for 3 days at 0. 3 mm.
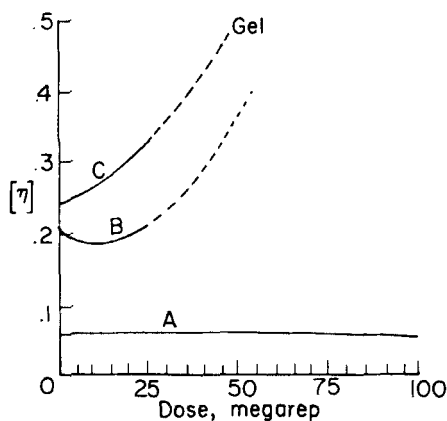
Fig. 21. Effect of irradiation on intrinsic viscosity of poly(2, 2-dimethyltrimethylene adipate) $-CH_2-C(CH_3)_2-CH_2-OCO-(CH_2)_4-OCO-_n$. See Table 24.

Table 24. Effect of Irradiation on Intrinsic Viscosity of Poly(2, 2-dimethyltrimethylene adipate) (See Fig. 21)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.069[a]	0.213[b]	0.235[c]
5	0.065	0.204	0.245
10	0.065	0.185	0.285
25	0.055	0.214	0.310
50	0.068	Gel	Gel
100	0.053	Gel	Gel

[a]At 220°C for 6 hr at 1 atm.
[b]At 220°C for 6 hr at 1 atm, then for 2 days at 0.3 mm.
[c]At 220°C for 6 hr at 1 atm, then for 3 days at 0.3 mm.
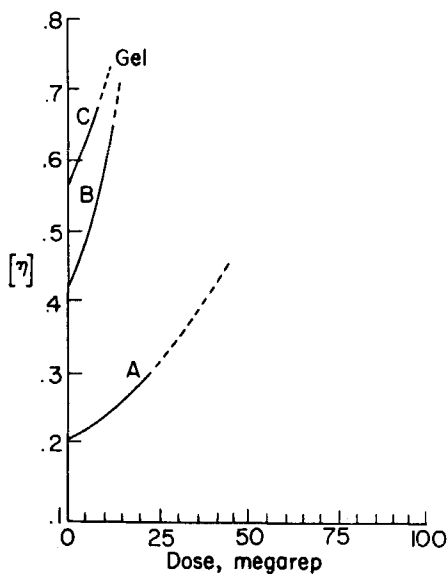
Fig. 22. Effect of irradiation on intrinsic viscosity of poly(2, 2-dimethyltrimethylene azelate) $+CH_2$—$C(CH_3)_2$—CH_2—OCO—$(CH_2)_7$—$OCO]_{\overline{n}}$. See Table 25.

Table 25. Effect of Irradiation on Intrinsic Viscosity of Poly(2, 2-dimethyltrimethylene azelate) (See Fig. 22)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0. 208[a]	0. 412[b]	0. 582[c]
5	0. 246	0. 476	0. 642
10	0. 220	0. 666	Gel
25	0. 318	Gel	Gel
50	Gel	Gel	Gel
100	Gel	Gel	Gel

[a]At 220°C for 6 hr at 1 atm.
[b]At 220°C for 6 hr at 1 atm, then for 1 day at 0. 3 mm.
[c]At 220°C for 6 hr at 1 atm, then for 4 days at 0. 3 mm.
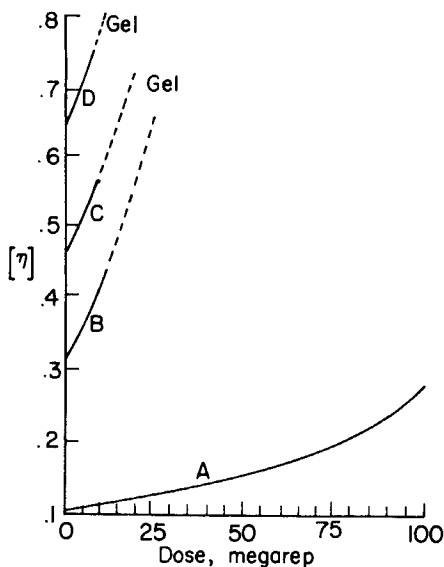
Fig. 23. Effect of irradiation on intrinsic viscosity of poly(2, 2-dimethyltrimethylene sebacate) $+CH_2-C(CH_3)_2-CH_2-OCO-(CH_2)_8-OCO+_n$. See Table 26.

Table 26. Effect of Irradiation on Intrinsic Viscosity of Poly(2, 2-dimethyltrimethylene sebacate) (See Fig. 23)

Dose, Mrep	Intrinsic viscosity, $[\eta]$			
	A	B	C	D
0	0.110[a]	0.308[b]	0.470[c]	0.621[d]
5	0.108	0.341	0.502	0.708
10	0.114	0.428	0.560	0.738
25	0.120	Gel	Gel	Gel
50	0.132	Gel	Gel	Gel
100	0.284	Gel	Gel	Gel

[a] At 220°C for 6 hr at 1 atm.
[b] At 220°C for 6 hr at 1 atm, then for 1 day at 0.3 mm.
[c] At 220°C for 6 hr at 1 atm, then for 3 days at 0.3 mm.
[d] At 220°C for 6 hr at 1 atm, then for 4 days at 0.3 mm.
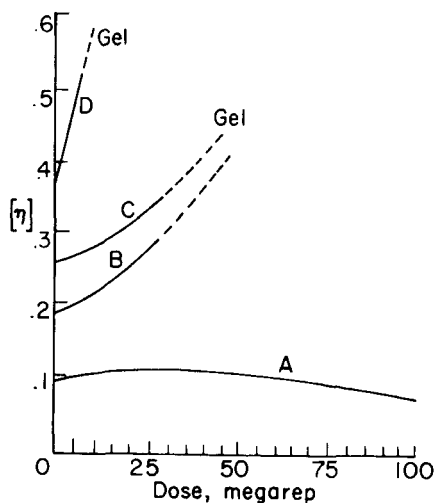
Fig. 24. Effect of irradiation on intrinsic viscosity of poly(2, 2-di-ethyltrimethylene succinate) $\{CH_2-C(C_2H_5)_2-OCO-(CH_2)_2-OCO\}_n$.
See Table 27.

Table 27. Effect of Irradiation on Intrinsic Viscosity of Poly(2, 2-diethyltrimethylene succinate) (See Fig. 24)

Dose, Mrep	Intrinsic viscosity, $[\eta]$			
	A	B	C	D
0	0. 098[a]	0. 193[b]	0. 280[c]	0. 385[d]
5	0. 108	0. 220	0. 259	0. 538
10	0. 120	0. 246	0. 275	Gel
25	0. 105	0. 282	0. 321	Gel
50	0. 082	Gel	Gel	Gel
100	0. 096	Gel	Gel	Gel

[a] At 220°C for 10 hr at 1 atm.
[b] At 220°C for 10 hr at 1 atm, then for 1 day at 0. 5 mm.
[c] At 220°C for 10 hr at 1 atm, then for 2 days at 0. 5 mm.
[d] At 220°C for 10 hr at 1 atm, then for 4 days at 0. 5 mm.
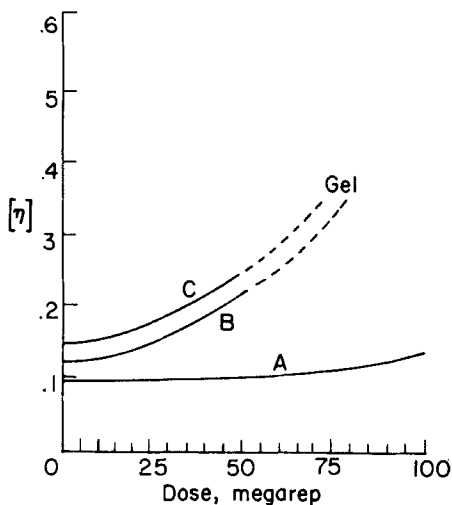
Fig. 25. Effect of irradiation on intrinsic viscosity of poly(2, 2-di-ethyltrimethylene adipate) $\{CH_2-C(C_2H_5)_2-CH_2-OCO-(CH_2)_4-OCO\}_{\overline{n}}$. See Table 28.

Table 28. Effect of Irradiation on Intrinsic Viscosity of Poly(2, 2-diethyltrimethylene adipate) (See Fig. 25)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.100[a]	0.128[b]	0.154[c]
5	0.099	0.158	0.173
10	0.094	0.144	0.180
25	0.110	0.160	0.184
50	0.104	0.182	0.224
100	0.115	Gel	Gel

[a]At 220°C for 10 hr at 1 atm.
[b]At 220°C for 10 hr at 1 atm, then for 3 days at 0.5 mm.
[c]At 210°C for 12 hr at 1 atm, then for 3 days at 0.3 mm.
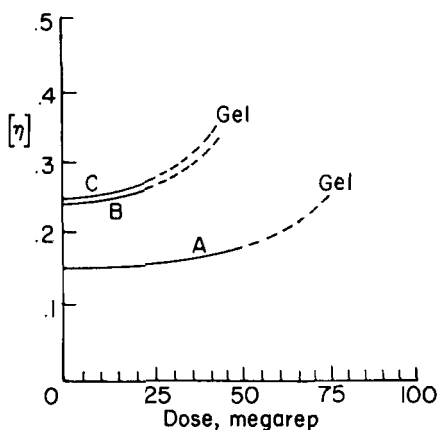
Fig. 26. Effect of irradiation on intrinsic viscosity of poly(2, 2-di-
ethyltrimethylene azelate) $\left[CH_2-C(C_2H_5)_2-CH_2-OCO-(CH_2)_7-OCO\right]_n$.
See Table 29.

Table 29. Effect of Irradiation on Intrinsic Viscosity of Poly(2, 2-
diethyltrimethylene azelate) (See Fig. 26)

Dose Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.166[a]	0.240[b]	0.246[c]
5	0.166	0.278	0.240
10	0.166	0.268	0.239
25	0.164	0.301	0.284
50	0.184	Gel	Gel
100	Gel	Gel	Gel

[a]At 200°C for 12 hr at 1 atm.
[b]At 220°C for 10 hr at 1 atm, then for 2 days at 0.5 mm.
[c]At 220°C for 10 hr at 1 atm, then for 3 days at 0.5 mm.
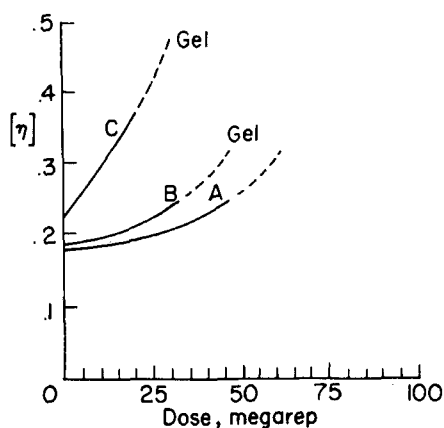
Fig. 27.   Effect of irradiation on intrinsic viscosity of poly(2, 2-di-ethyltrimethylene sebacate) $+CH_2-C(C_2H_5)_2-CH_2-OCO-(CH_2)_8-OCO+_n$.
See Table 30.

Table 30.   Effect of Irradiation on Intrinsic Viscosity of Poly(2, 2-diethyltrimethylene sebacate) (See Fig. 27)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0. 198[a]	0. 191[b]	0. 230[c]
5	0. 184	0. 221	0. 240
10	0. 186	0. 209	0. 208
25	0. 204	0. 192	0. 459
50	0. 274	Gel	Gel
100	Gel	Gel	Gel

[a]At 220°C for 6 hr at 1 atm.
[b]At 220°C for 6 hr at 1 atm, then for 2 days at 0. 3 mm.
[c]At 220°C for 6 hr at 1 atm, then for 4 days at 0. 3 mm.
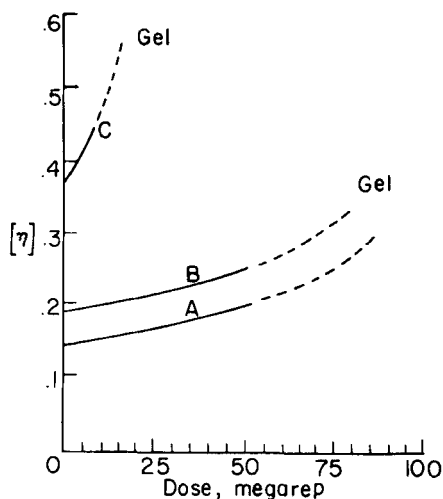
Fig. 28. Effect of irradiation on intrinsic viscosity of poly(3-methyl-pentamethylene succinate) $+(CH_2)_2-CH(CH_3)-(CH_2)_2-OCO-(CH_2)_2-OCO+_n$.
See Table 31.

Table 31. Effect of Irradiation on Intrinsic Viscosity of Poly(3-methylpentamethylene succinate) (See Fig. 28)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0. 151[a]	0. 189[b]	0. 375[c]
5	0. 140	0. 196	0. 412
10	0. 155	0. 211	0. 486
25	0. 183	0. 220	Gel
50	0. 194	0. 239	Gel
100	Gel	Gel	Gel

[a]At 220°C for 12 hr at 1 atm.
[b]At 220°C for 12 hr at 1 atm, then for 1 day at 0. 3 mm.
[c]At 220°C for 10 hr at 1 atm, then for 4 days at 0. 5 mm.
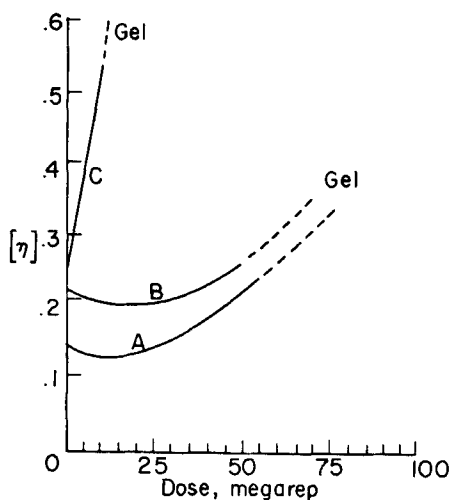
Fig. 29. Effect of irradiation on intrinsic viscosity of poly(3-methyl-pentamethylene adipate) $+(CH_2)_2-CH(CH_3)-(CH_2)_2-OCO-(CH_2)_4-OCO\}_n$. See Table 32.

Table 32. Effect of Irradiation on Intrinsic Viscosity of Poly(3-methylpentamethylene adipate) (See Fig. 29)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.248[a]	0.318[b]	0.343[c]
5	0.232	0.316	0.482
10	0.212	0.289	0.642
25	0.259	0.297	Gel
50	0.310	0.342	Gel
100	Gel	Gel	Gel

[a]At 220°C for 5 hr at 1 atm, then for 12 hr at 0.3 mm.
[b]At 220°C for 10 hr at 1 atm, then for 4 days at 0.3 mm.
[c]At 220°C for 10 hr at 1 atm, then for 6 days at 0.3 mm.
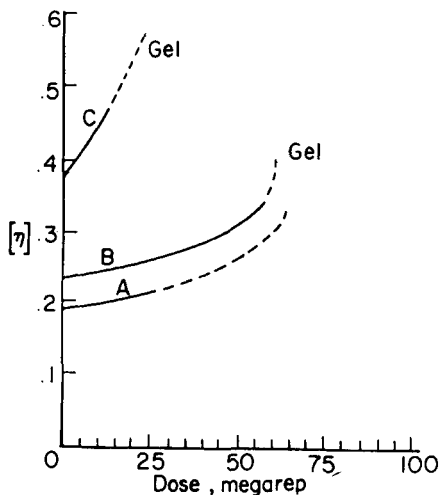
Fig. 30. Effect of irradiation on intrinsic viscosity of poly(3-methyl-pentamethylene azelate) $+(CH_2)_2-CH(CH_3)-(CH_2)_2-OCO-(CH_2)_7-OCO+_{\overline{n}}$.
See Table 33.

Table 33. Effect of Irradiation on Intrinsic Viscosity of Poly(3-methylpentamethylene azelate) (See Fig. 30)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.195[a]	0.244[b]	0.388[c]
5	0.183	0.240	0.431
10	0.203	0.248	0.462
25	0.207	0.248	Gel
50	Gel	0.354	Gel
100	Gel	Gel	Gel

[a]At 220°C for 6 hr at 1 atm.
[b]At 220°C for 6 hr at 1 atm, then for 1 day at 0.3 mm.
[c]At 220°C for 6 hr at 1 atm, then for 3 days at 0.3 mm.
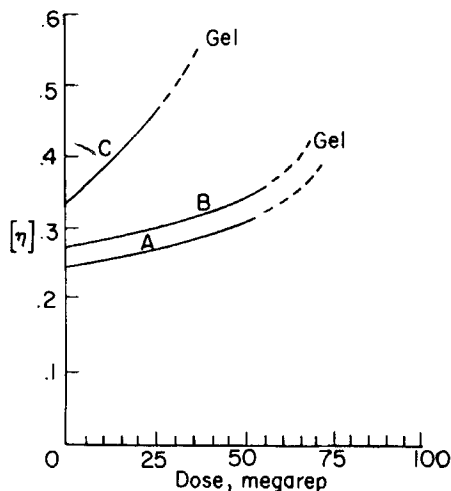
Fig. 31. Effect of irradiation on intrinsic viscosity of poly(3-methyl-
pentamethylene sebacate) $+(CH_2)_2-CH(CH_3)-(CH_2)_2-OCO-(CH_2)_8-OCO+_n$.
See Table 34.

Table 34. Effect of Irradiation on Intrinsic Viscosity of Poly(3-
methylpentamethylene sebacate) (See Fig. 31)

Dose, Mrep	Intrinsic viscosity, $[\eta]$		
	A	B	C
0	0.244[a]	0.262[b]	0.332[c]
5	0.269	0.264	0.365
10	0.250	0.294	0.388
25	0.282	0.298	0.467
50	0.313	0.339	Gel
100	Gel	Gel	Gel

[a]At 220°C for 10 hr at 1 atm.
[b]At 220°C for 24 hr at 1 atm, then for 12 hr at 0.3 mm.
[c]At 220°C for 10 hr at 1 atm, then for 24 hr at 0.5 mm.
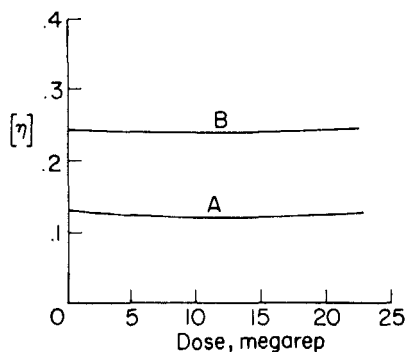
Fig. 32. Effect of irradiation on intrinsic viscosity of poly(penta-
methylene-2, 3-diphenyl succinate)
$+(CH_2)_5-OCO-CH(C_6H_5)-CH(C_6H_5)-OCO-]_{\overline{n}}$. See Table 35.
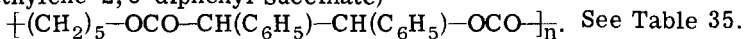
Table 35. Effect of Irradiation on Intrinsic Viscosity of Poly(penta-
methylene-2, 3-diphenyl succinate) (See Fig. 32)

Dose, Mrep	Intrinsic viscosity, $[\eta]$	
	A	B
0	0. 126[a]	0. 242[b]
5	0. 120	0. 240
10	0. 110	0. 246
15	0. 123	0. 246
20	0. 099	0. 244
25	0. 113	0. 245

[a]At 240°C for 6 hr at 1 atm.
[b]At 240°C for 5 hr at 1 atm, then for 2 days at 0. 3 mm.
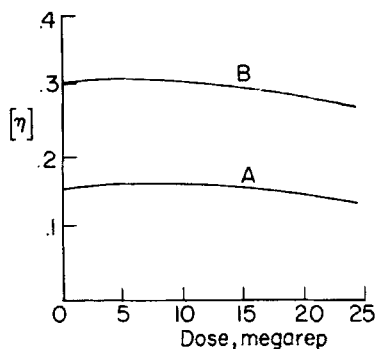
Fig. 33. Effect of irradiation on intrinsic viscosity of poly(3-methyl-pentamethylene-3-methyl adipate)

$+(CH_2)_2-CH(CH_3)-(CH_2)_2-OCO-(CH_2)_2-CH(CH_3)-(CH_2)-CH-OCO\}_n$.
See Table 36.

Table 36. Effect of Irradiation on Intrinsic Viscosity of Poly(3-methylpentamethylene-3-methyl adipate) (See Fig. 33)

Dose, Mrep	Intrinsic viscosity, $[\eta]$	
	A	B
0	0.150[a]	0.294[b]
5	0.160	0.308
10	0.150	0.288
15	0.152	0.278
20	0.148	0.274
25	0.138	0.270

[a]At 220°C for 6 hr at 1 atm.
[b]At 200°C for 6 hr at 1 atm, then for 3 days at 0.3 mm.
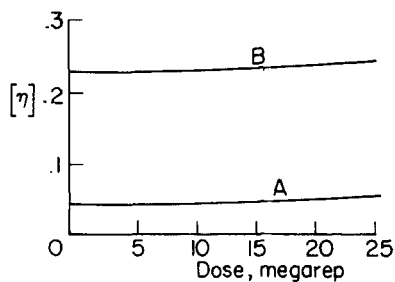
Fig. 34. Effect of irradiation on intrinsic viscosity of poly(2, 2-dimethyltrimethylene-3, 3-dimethyl glutarate)
$\{CH_2-C(CH_3)_2-CH_2-OCO-CH_2-C(CH_3)_2-CH_2-OCO\}_n$.
See Table 37.
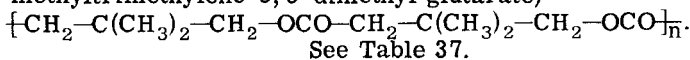
Table 37. Effect of Irradiation on Intrinsic Viscosity of Poly(2, 2-dimethyltrimethylene-3, 3-dimethyl glutarate) (See Fig. 34)

Dose, Mrep	Intrinsic viscosity, $[\eta]$	
	A	B
0	0.045[a]	0.232[b]
5	0.040	0.228
10	0.038	0.224
15	0.041	0.230
20	0.051	0.235
25	0.060	0.238

[a]At 220°C for 6 hr at 1 atm.
[b]At 220°C for 6 hr at 1 atm, then for 2 days at 0.3 mm.
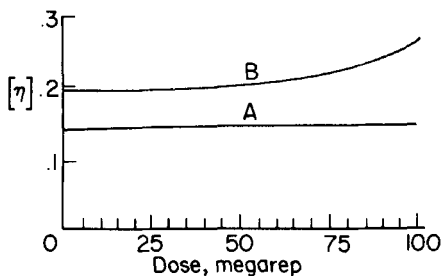
Fig. 35.   Effect of irradiation on intrinsic viscosity of poly(penta-methylene-2-methyl succinate) $-(CH_2)_5-OCOCH_2CH(CH_3)COO-_n$. See Table 38.

Table 38.   Effect of Irradiation on Intrinsic Viscosity of Poly(penta-methylene-2-methyl succinate) (See Fig. 35)

Dose, Mrep	Intrinsic viscosity, $[\eta]$	
	A	B
0	0.146[a]	0.184[b]
5	0.140	0.186
10	0.142	0.189
25	0.138	0.183
50	0.158	0.200
100	0.156	0.261

[a]At 220°C for 6 hr at 1 atm.
[b]At 220°C for 6 hr at 1 atm, then for 6 hr at 0.5 mm.
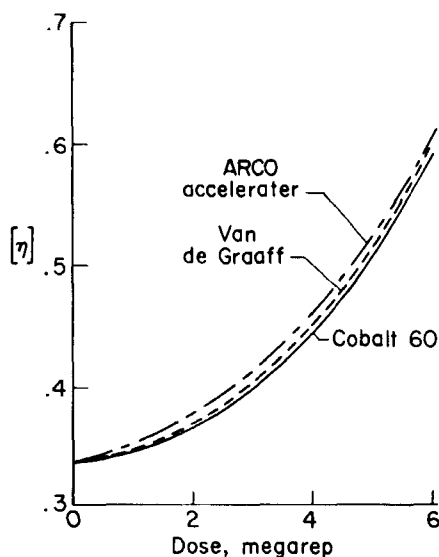
Fig. 36. Effect of dose rate and source on intrinsic viscosity of poly-(tetramethylene sebacate) (absence of oxygen at pressure of 1×10^{-7} mm Hg). See Table 39.

Table 39. Effect of Dose Rate and Source on Intrinsic Viscosity of Poly(tetramethylene sebacate) (See Fig. 36)

Source of irradiation	Dose, Mrep	Intrinsic viscosity
Cobalt 60	0	0.340
	2.0	0.375
	3.0	0.410
	4.2	0.475
	6.0	Gel
Van de Graaf (2 MeV)	0	0.340
At 50 μA	2.0	0.378
At 100 μA	4.0	0.470
At 25 μA	5.0	0.536
At 25 μA	6.0	Gel
ARCO accelerator (8 MeV)	0	0.340
At 50 μA	2.0	0.376
At 50 μA	3.8	0.472
At 50 μA	5.8	Gel

Influence of Air and Film Thickness on Effects of Ionizing Radiation

Six films of poly(tetramethylene sebacate) of thicknesses varying from 0.1 to 2.0 mm were introduced into glass tubes, and the tubes were then evacuated at room temperature for 72 hr at a pressure of 1×10^{-7} mm Hg to remove air and traces of volatile matter. Air, which had been filtered through glass wool, was admitted to two of the tubes to a pressure of 2 mm Hg, and to three of the tubes to a pressure of 760 mm Hg; all tubes were then sealed and irradiated

Table 40. Effect of Air Pressure and Film Thickness on Intrinsic Viscosity of Poly(tetramethylene sebacate) (See Fig. 37)

Film	Thickness, mm	Air pressure, mm	Dose, Mrep	$[\eta]$
A	0.10	760	0	0.340
			2.0	0.300
			4.0	0.285
			6.0	0.281
B	0.25	760	0	0.340
			3.0	0.320
			4.0	0.315
			5.4	0.315
C	2.00	760	0	0.340
			2.3	0.340
			4.0	0.368
			4.8	0.390
			5.8	0.460
D	0.25	2.00	0	0.340
			2.3	0.350
			4.0	0.382
			5.0	0.428
			6.0	0.497
E	2.00	2.00	0	0.340
			2.0	0.350
			4.0	0.395
			5.0	0.454
			6.0	0.521
F	2.00	5×10^{-6}	0	0.340
			2.0	0.375
			3.0	0.411
			4.4	0.475
			6.0	Gel

within a dose range 2-6 Mrep. The weight of the polymer was 0.05 g, and the volume of the tubes was 50 ml. The influence of air and film thickness on the radiation-induced changes in the intrinsic viscosity is given in Table 40 and graphically shown in Fig. 37.
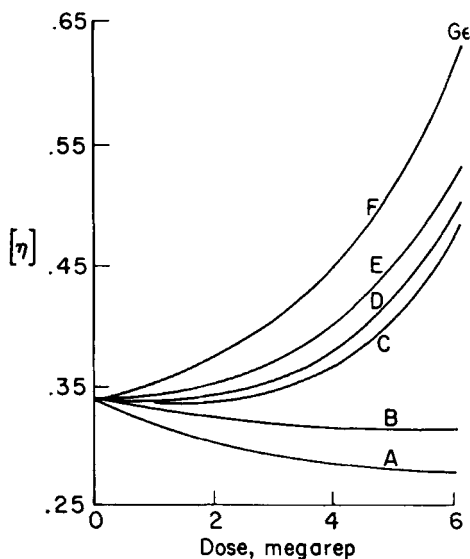
Fig. 37. Effect of air pressure and film thickness on intrinsic vis-cosity of poly(tetramethylene sebacate). See Table 40.

Influence of Orientation on Effect of Ionizing Radiation

Poly(tetramethylene sebacate) ($[\eta]$ 0.358), which exhibits marked crystallinity, was melt-spun to monofilaments of about 0.1 mm. Parts of these monofilaments were stretched at room temperature to three times their original length, and annealed at 60°C for 8 hr, after which they exhibited marked birefringence under cross Nicol prisms. One-tenth-gram samples of the unstretched and stretched filaments were placed in 50-ml glass tubes, and the tubes were then evacuated at a pressure of 1×10^{-7} mm Hg for 72 hr, after which they were irradiated at 25°C with dosages up to 13 Mrep. Another set of tubes was heated to 80°C before and during the irradiation so that the polymer was in the amorphous state. The intrinsic vis-cosities before and after irradiation were measured. The data are summarized in Table 41 and shown graphically in Fig. 38.

Table 41. Effect of Orientation on Intrinsic Viscosity of Poly(tetra-
methylene sebacate) (See Fig. 38)

Dose, Mrep	$[\eta]$
Unoriented filaments	
0	0.358
2	0.410
3	0.440
4	0.512
5	0.648
7	Gel
10	Gel
Oriented filaments	
0	0.358
3	0.420
5	0.462
7	0.521
10	0.607
13	Gel
Melted polymer	
0	0.358
4	Gel
6	Gel
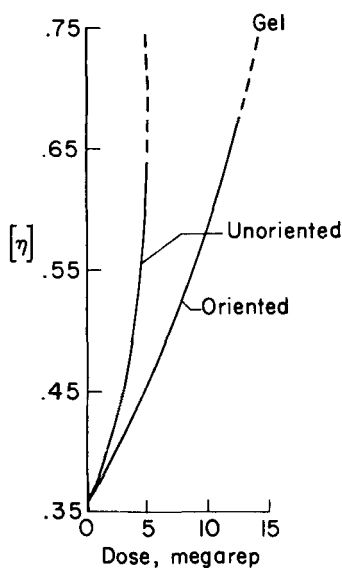
Fig. 38. Effect of orientation on intrinsic viscosity of poly(tetra-
methylene sebacate). See Table 41.

Effect of Postheating on Irradiated Poly(tetramethylene sebacate)

One-tenth-gram samples of irradiated poly(tetramethylene
sebacate) monofilaments ($[\eta]$ 0.358) were sealed in 50-ml tubes at
a pressure of 1×10^{-7} mm Hg after the tubes had been evacuated
for 72 hr. The samples were then subjected to a 3-Mrep dose of
irradiation, which is below that found to produce a gel. The irradiat-
ed monofilaments, while still in the sealed tubes, were heated for
various periods of time at 68°C, which is the melting point of the
polymer. Intrinsic viscosities were measured before and after the
heating periods, and the results are given in Table 42 and graphically
presented in Fig. 39.

Changes in Elemental Compositions of Polymer on Irradiation

Effect of Thickness on Loss of Weight of Irradiated Sample.
Films of poly(tetramethylene sebacate) having thicknesses of 0.25,
0.50, and 0.75 mm were placed in 25-ml tubes, evacuated at a pres-
sure of 1×10^{-7} mm Hg for 8 hr, and then irradiated. The weight
of the films was approximately 0.1 g. After irradiation the tubes
were opened and the films were weighed. The films were then de-
gassed at room temperature at 1×10^{-7} mm Hg for 48-72 hr to

Table 42.   Effect of Heating Irradiated Poly(tetramethylene
sebacate)[a] (See Fig. 39)

Hours heated at 68°C in vacuo	$[\eta]$
Unoriented filaments	
0	0.440
5	0.445
15	0.451
25	0.454
30	0.454
45	0.454
Oriented filaments	
0	0.420
5	0.431
10	0.437
15	0.441
25	0.444
30	0.446
45	0.446

[a]Dosage: 3 Mrep, at pressure of 1×10^{-7} mm Hg.
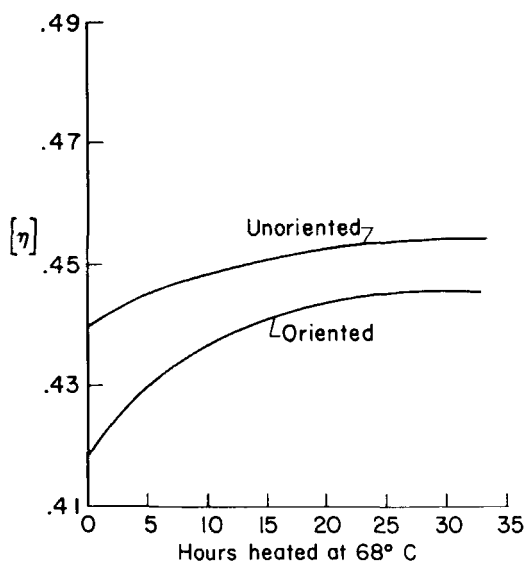
Fig. 39. Effect of heating irradiated oriented and unoriented poly-(tetramethylene sebacate) filaments. See Table 42.

constant weight. The per cent weight losses for the poly(tetra-methylene sebacate) films are summarized in Table 43.

Elemental Analysis of Polyesters Before and After Irradiation. Two-gram samples of 0.25-mm films of poly(tetramethylene sebacate) and poly(ethylene succinate) were sealed in 25-ml tubes and evacuated at 1×10^{-7} mm Hg for 24 hr, irradiated, and then heated to destroy trapped radicals. Similar unsealed samples were irradiated while exposed to air. Analyses for carbon, hydrogen, and oxygen were made by Midwest Microlab, Inc., Indianapolis, Indiana, on the samples of the polyesters before and after irradiation, and the results obtained are summarized in Table 44.

Analysis of Gases Resulting from Irradiation of Polyesters. A sample of the polyester was introduced into a 25-ml irradiation cell sealed with a vacuum stopcock, evacuated at 1×10^{-7} mm Hg for 12 hr, and then irradiated to the dosages indicated in Table 45. After irradiation, the cell was cooled to within the range -8 to $-10°C$ for 2 hr to condense any liquid products. The gaseous products were then allowed to expand at room temperature from the irradiation cell into a 300-ml collection bulb previously evacuated to 10^{-6} mm Hg, and a mass spectrographic analysis was performed by using a Consolidated Engineering Corp. Type 21-103A spectro-

Table 43. Loss in Weight of Poly(tetramethylene sebacate) polymer[a]
Due to Irradiation

		Weight loss, %	
Film thickness, mm	Dose, Mrep	After irradiation	After post evacuation
0.25	1	1.5	1.52
	5	3.0	3.16
	20	4.8	4.92
0.50	1	0.8	1.1
	5	1.5	1.7
	20	1.8	2.01
0.75	1	0.1	0.63
	5	0.6	1.20
	20	0.9	1.84

[a]$[\eta] = 0.340$.

Table 44. Elemental Analyses of Polyesters before and after Irradiation

	Element	Elemental analyses, %			
Polymer		Theoretical	Before irradiation	After irradiation at 10^{-7} mm	After irradiation in air
Poly(tetramethylene	C	65.62	65.64	65.68	60.27
sebacate) ($[\eta]$ 0.340;	H	9.36	9.33	9.56	8.67
dose 400 Mrep)	O	25.01	25.10	24.76	31.06
Poly(ethylene succinate)	C	50.00	49.97	51.17	45.65
($[\eta]$ 0.326; dose	H	5.55	5.51	5.91	5.18
50 Mrep)	O	44.45	44.52	42.92	49.17

meter. The data in mole per cent are reported for poly(ethylene succinate), poly(tetramethylene sebacate), and poly(decamethylene sebacate) in Table 45, along with the data of other compounds, such as poly(methyl methacrylate) [26], caprylic acid, sebacic acid, and cetyl palmitate, taken from the literature [27-28].

Table 45. Gases from Irradiation of Polymers and Reference Compounds

Substance	Dose, Mrep	Gas, mole %				
		H_2	CO	CO_2	RH^a	Other
Poly(ethylene succinate),[c] $[\eta]$ 0.326	50	44.0	16.5	9.7	7.4[d]	22.4
Poly(tetramethylene sebacate),[c] $[\eta]$ 0.340	4	49.2	26.6	17.1	4.98	3.12
Poly(tetramethylene sebacate),[c] $[\eta]$ 0.340	22	49.6	26.2	18.0	4.00	2.2
Poly(decamethylene sebacate),[c] $[\eta]$ 0.270	10	61.9	14.8	13.6	5.8	3.9
Poly(methyl methacrylate) [26]	22	44.1	22.8	18.8	6.0	8.3[e]
Caprylic acid [27, 28]	—	33.0	9.0	51.0	f	7.0
Sebacic acid [27, 28]	92	26.3	2.1	68.9	f	2.7
Cetyl palmitate [refs. 27, 28]	—	85.0	3.0	4.0	3.6	4.4

[a] Includes the volatile hydrocarbons to C_3H_8.
[b] Includes H_2O, higher hydrocarbons, O_2, N_2, and so forth.
[c] 0.1-g samples, 0.25 mm thick.
[d] For poly(ethylene succinate), the sum of RH for $CH_4 = 0.5$, $C_2H_6 = 0.7$, and $C_3H_8 = 6.2$ totals 7.4 mole%.
[e] Nitrogen accounts for 7.3 mole%.
[f] RH value included in "other".

Irradiation Grafting of Styrene and Divinylbenzene to Polymers and Effects on Certain Properties

The polyester was melted at temperatures from 60 to 65°C in an inert atmosphere in a dry box, and a weighed amount of monomeric redistilled styrene or divinylbenzene was stirred into the melt until it appeared to be homogeneous; then the mixture was transferred to an irradiation cell and immediately cooled in a dry ice-acetone mixture. The irradiation cell and contents were evacuated for 2 hr at 10^{-7} mm Hg while cooled in liquid nitrogen. The cell was then sealed and exposed to irradiation, and the changes in a number of properties after radiation at the specific doses were measured.

Effect of Irradiation on Intrinsic Viscosity of Mixtures of Polyesters and Divinylbenzene. The intrinsic viscosities of irradiated mixtures of poly(tetramethylene sebacate) and divinylbenzenes at dosages below the gelation doses are given in Table 46 and graphically presented in Fig. 40. The changes in the viscosities of mix-
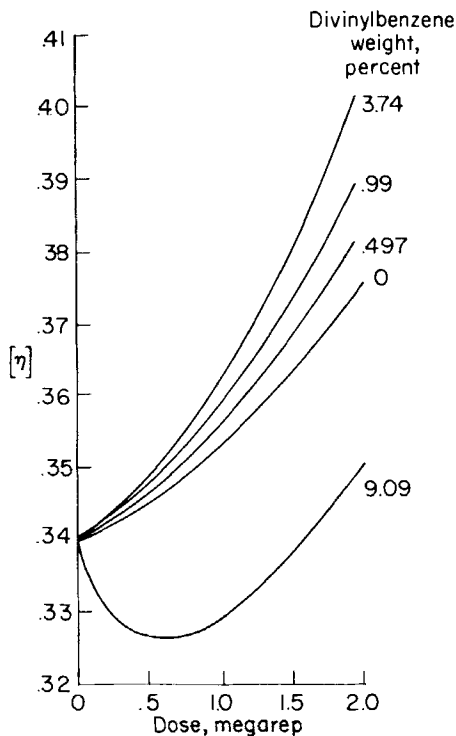
Fig. 40. Intrinsic viscosity of mixtures of poly(tetramethylene sebacate) and divinylbenzene. See Table 46.

Table 46. Intrinsic Viscosity of Mixtures of Poly(tetramethylene sebacate and Divinylbenzene (See Fig. 40)

Polymer weight, g	Divinyl benzene weight, g	Actual divinyl-benzene weight, %	Dose, Mrep	$[\eta]$
100	0	0	0	0.340
			0.5	0.345
			1.0	0.354
			2.0	0.375
99.5	1.1	0.497	0	0.340
			0.5	0.347
			1.0	0.357
			2.0	0.383
99.0	2.0	0.990	0	0.339
			0.5	0.348
			1.5	0.374
			2.0	0.391
96.0	8.0	3.74	0	0.337
			0.5	0.349
			1.0	0.364
			1.5	0.384
			2.0	0.403
90.0	20.0	9.09	0	0.336
			0.25	0.338
			0.50	0.325
			0.75	0.327
			1.00	0.330
			1.25	0.335
			1.50	0.339
			1.75	0.344

tures of divinylbenzene and poly(ethylene sebacate) after irradiation are qualitatively and quantitatively so similar to viscosity changes of the tetramethylene ester that they do not need to be reported separately. The divinylbenzene used in these experiments contained 50.2% mixed divinylbenzenes and 49.8% mixed ethyl vinylbenzenes, and 2 g of the mixture were used when 1 g of divinylbenzene was required. In one case (Table 47), pure p-divinylbenzene was used.

Table 47. Effect of Irradiation on Solubility of Mixtures of
  Poly(tetramethylene sebacate) and Styrene (See Fig. 41)

Polymer weight, g	Divinylbenzene weight, g	Actual divinylbenzene weight, %	Dose, Mrep	Weight extracted, %
100	0	0	4	100
			12	79
			30	59
			50	44
			60	38
99.5	1.1	0.497	4	95
			16	69.6
			37	45
			50	35.1
99.0	2	0.99	4	76.1
			20	53.5
			36	39.1
			49	29
96.0	8	3.74	4	71
			8.5	62
			25	43
			40	29
			45	26
			50	23
90.0	20	9.09	4	60
			7.3	52
			13	32
			20	20
			32	61
50.0	50	33.3	1	40
			2	16
			4	32
			11	43
			41	53
91.0	0	9[a]	7.5	42.5
			15	24.2
			20	16.4
			25	9.8

[a]100% p-divinylbenzene.

Effect of Irradiation on Solubility of a Mixture of Polyester and Divinylbenzene or Styrene. The mixtures were prepared as described previously and exposed to irradiation for the period of time indicated. The sample was then submitted to extraction. A sample weighing from 0.1 to 0.2 g was placed in a Soxhlet microextractor (thimble volume about 7 ml) and continuously extracted with chloroform for 24 hr. The extracted sample was then dried to constant weight in a vacuum oven at 40°C, and the amount extracted was considered as the soluble portion of the mixture. The solubility data for irradiated mixtures of divinylbenzene and poly(tetramethylene sebacate) are given in Table 47 and graphically presented in Fig. 41; for mixtures of poly(tetramethylene sebacate) and styrene, in Table 48 and Fig. 42; and for mixtures of poly(ethylene succinate) and divinylbenzene, in Table 49 and Fig. 43.

Swelling Index of Irradiated Polymers. A 0.050-g sample of an irradiated polymer was immersed in 50 ml of chloroform at room temperature until equilibrium was reached and no further volume change was noted in the swollen polymer. The time required varied from 4 to 8 days. The swollen polymer was then separated from excess solvent and weighed in a tightly closed weighing bottle. The swelling index was calculated by using the formula $(W_f - W_i)/W_i$, where W_f is the weight of the swollen polymer and W_i is the initial weight of the polymer before swelling. The lower the swelling index, the higher is the extent of cross-linking. The data for the mixture of poly(tetramethylene sebacate) and divinylbenzene are summarized in Table 50 and represented graphically in Fig. 44; the data for the mixture of poly(ethylene succinate) and divinylbenzene are given in Table 49.
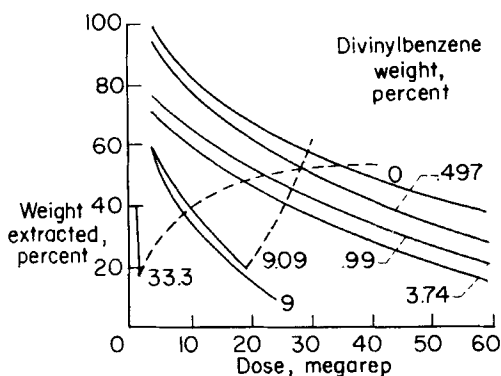
Fig. 41. Effect of irradiation on solubility of mixtures of poly(tetramethylene sebacate) and divinylbenzene. See Table 47.

Table 48. Effect of Irradiation on Solubility of Mixtures of
Poly(tetramethylene sebacate) and Styrene (See Fig. 42)

Styrene, %	Dose, Mrep	Weight extracted, %
0	4	100
	12	79
	30	59
	50	44
	60	38
1.0	9	80
	24	63
	33	56
4.0	4	100
	11	84
	22.5	70
	35	58
	45	48
10.0	4	100
	15	84
	31	66
	50	54
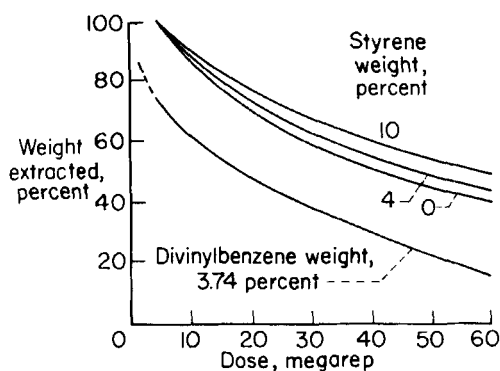
Fig. 42. Effect of irradiation on solubility of mixtures of poly(tetra-
methylene sebacate) and styrene. See Table 48.

Table 49. Swelling Index of Irradiated Mixtures of Poly(ethylene succinate) and Divinylbenzene[a] (See Fig. 43)

Divinylbenzene weight, %	Dose, Mrep	Weight extracted, %	$\dfrac{W_f - W_i}{W_i}$
0	10	100	Soluble
	25	100	Soluble
	50	100	Soluble
	100	100	Soluble
	200	100	Soluble
	400	100	Soluble
1.96	2	100	Soluble
	20	100	Soluble
	50	100	Soluble
	100	100	Soluble
	200	87	85.5
	250	64	10.7
	300	58	1.1
	380	55	1.0
	400	55	1.1
4.75	50	74	3.8
	60	80	2.6
	100	58	1.0
	200	44	1.10
	320	40	1.09
	380	39	1.0
9.09	50	55	1.8
	100	40	1.0
	200	35	1.0
	300	34	0.9
	400	32	1.0

[a] W_i is initial weight of unswollen polymer; W_f is weight of swollen polymer.
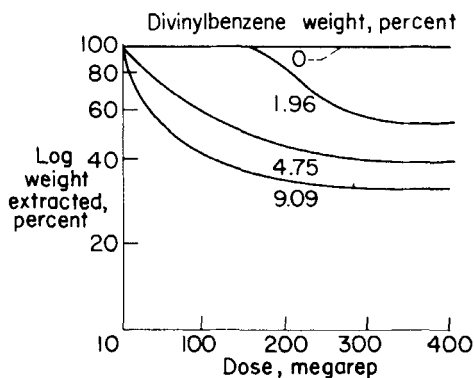
Fig. 43. Effect of irradiation on solubility of mixtures of poly-
(ethylene succinate) and divinylbenzene. See Table 49.
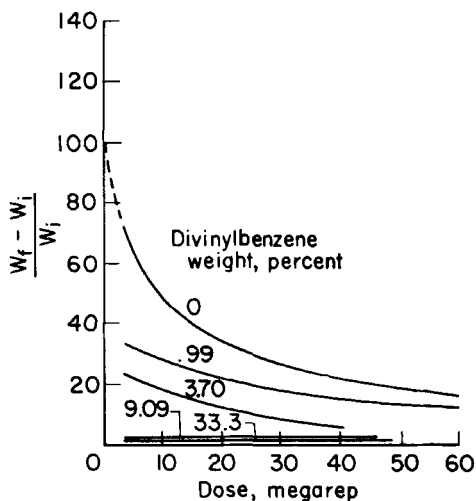
Fig. 44. Swelling index of irradiated mixtures of poly(tetramethy-
lene sebacate) and divinylbenzene. See Table 50.

Table 50. Swelling Index of Irradiated Mixtures of Poly(tetra-
methylene sebacate) and Divinylbenzene[a] (See Fig. 44)

Divinylbenzene weight, %	Dose, Mrep	$\dfrac{W_f - W_i}{W_i}$
0	4	Soluble
	12	43.3
	30	27.1
	60	16.5
0.99	4	33
	20	24
	36	16
	50	14
3.70	4	23.7
	8.5	18.3
	25	10.1
	50	6.0
9.09	4	2.3
	7.3	2.2
	13	2.3
	32	2.2
	55	2.2
33.3	4	0.96
	11	1.02
	40	1.02
	55	1.01

[a]W_i is initial weight of unswollen polymer; W_f is weight of
swollen polymer.

Infrared Spectra

A Perkin-Elmer double-beam infrared spectrophotometer, Model
21, with a NaCl prism was used to obtain the spectral data. Opera-
ting conditions were selected to give a compromise between resolu-
tion and noise level. The polyester samples used were prepared in
film form by casting solutions of the polymer in chloroform on new
glass plates. The solvent was then allowed to evaporate at room
temperature for 24 hr, after which the samples were heat-treated
in an oven from 63 to 64°C for 8-10 hr. The film thicknesses used
ranged from 0.8 to 1.8 mm. The films were removed from the

glass and mounted on small cardboard frames with the film being the "window" of the frame. To remove volatiles from the samples, they were evacuated at 10^{-6} mm Hg for 8-10 hr at room temperature, and the spectra were recorded before and after irradiation in vacuo (10^{-6} mm Hg) and in air.

Poly(tetramethylene sebacate) was irradiated to doses of 50, 150, and 250 Mrep, and the spectra recorded before and after irradiation were compared. Complete information required to interpret the spectra of saturated aliphatic polyesters does not exist in the published literature. Therefore, an additional study was undertaken at the University of Notre Dame on the spectra of this class of polyesters, and assignments of as many of the absorption bands as possible were made with the help of published data on related compounds and other polymers.

Diagnostic Saponification of Irradiated Poly(tetramethylene sebacate)

The poly(tetramethylene sebacate) ($[\eta]$ 0.420) was prepared from 101 g of sebacic acid (0.5 mole) and 45.9 g of butanediol-1,4 (0.51 mole) by reaction at 250°C for 5 hr at 1 atm, then at 270°C for 72 hr at 0.1 mm Hg. Neutralization equivalent (N.E.) of sebacic acid was approximately 101 (206 ml of 0.4808 N KOH = 100.96 for a mol. wt. of 201.92). For irradiation, part of the molten polyester was cast under nitrogen into a thin rectangular sheet about 350 millimeters thick, sealed under nitrogen in a double layer of 1-mm-thick aluminum foil, and irradiated. The dose rate was 1.6 Mrep/min; the sample was maintained at about room temperature by contact with cooled metal blocks. The total dose was 250 Mrep, and the swelling index, $(W_f - W_i)/W_i$, was 0.76. Samples of the polymer before and after irradiation were saponified by the following procedures.

The unirradiated polymer was cut into small pieces, and 25.6 g was added to 42 g of KOH in 100 ml of 50% aqueous ethanol and refluxed in a nitrogen atmosphere for 72 hr. The homogeneous saponified mixture was diluted with 500 ml of distilled water, filtered, and passed through a 1-m column of Dowex 50 cation-exchange resin. The column contained 2.5-mole equivalents of the resin in the hydrogen form. Sodium cobalt-nitrate was used to test the resin-treated solution A for the presence of potassium ions. Four passes through the column were required before a potassium-free solution was obtained. Between passes, the column was allowed to drain and was then refilled with water, allowed to stand for 1 hr, and drained again. The drainings and washings were added to solution A. The washing was repeated three times; the column was then

regenerated with mixtures of 50% water and 50% concentrated HCl, and washed until free of chloride ions. Solution A, containing the carboxylic acids and the polyols, was then concentrated at a pressure of 15 mm Hg at a temperature from 25 to 30°C. When the volume was reduced to 200 ml, the acids precipitated and were then separated by filtration and washed by cold water. The washings and filtrate were combined to form solution B. To remove the last traces of acids, solution B was passed through a column of Dowex 2 anion ion exchange resin, and the deacidified solution C was collected. The column was filled with distilled water, allowed to stand for 2 hr, and drained. The washings were repeated three times and then were added to solution C. The carboxylic acids were eluted from the anion-exchange resin with 15% HCl, and the column was filled with distilled water twice and allowed to stand for 2 hr. The eludate and the washings were combined and then evaporated under reduced pressure (15 mm Hg), and the solid carboxylic acids were combined with the acids previously separated and dried in vacuo at 50°C to a constant weight of 19.9 g which is 98.5% of theory (N.E. 101, recrystalized m.p. 133°C).

The deacidified solution C was distilled in an 18-in. fractionating column to remove water and low-boiling materials, and then to isolate the butane-diol, which was recovered in a yield of 8.92 g which is 99.1% of theory (b.p. 229-230°C, n_D^{25} 1.443; lit b.p. 230°C, n_D^{25} 1.446).

An attempt was made to saponify 25.6 g of the irradiated polymers cut into small pieces with the same $KOH-H_2O-CH_3OH$ mixture used for the unirradiated sample, and very little saponification occurred in 30 hr; only surface pitting was evident on the polymer, and the saponification under these conditions was discontinued. Instead, the polymer was added to a solution of 42 g of KOH in 200 ml of water and heated to 160°C in an autoclave for 48 hr. This process resulted in a homogeneous solution which was diluted, when cool, with 500 ml of distilled water, filtered, and treated with ion-exchange resins, similarly to the saponified unirradiated polyesters. The recovered weight of tetramethylene glycol was 8.856 g, which is 98.4% of theory (b.p. 229-230°C, n_D^{25} 1.444). The weight of the polycarboxylic acids (m.p. 130.2°C), was 19.81 g, which is 98.1% of theory. The neutralization equivalent (19.28 ml of 0.5102 N KOH) was 101.65, which corresponds to a molecular weight of 203.3 for a dicarboxylic acid, 304.95 for a tricarboxylic acid, and 406.6 for a tetracarboxylic acid, or a mixture of 99.35% sebacic acid and 0.65% disebacic acid. The carboxylic acid fraction was recrystallized from water and dried; the recovered weight was 18.73 g (m.p. 133°C, N.E. 101). The filtrate was evaporated to dryness yielding 1.068 g. (N.E. 106.8, which corresponds to a mixture of 93.5% sebacic acid and 6.35% disebacic acid. The hydroxyl number was too small to measure.)

DISCUSSION

Effect of Irradiation on Intrinsic Viscosity of Saturated Linear Polyesters

When a polymer is subjected to ionizing radiation, either of two ultimate effects may result: (1) the cross-linking of the polymer chains observable first by an increase in molecular weight (or intrinsic viscosity), and, with increased radiation dose, by the formation of an insoluble network or gel, or (2) degradation as a result of scissions in the polymer chain producing a decrease in its intrinsic viscosity. Both processes occur simultaneously in many polymers, and the final observable effect depends on the ratio of the rates of the cross-linking reaction α to the scission reaction β in the specific polymer (pp. 80-83 of [1]). In the polyesters used in these studies, it would be expected that the cross-linking reaction α would occur by the coupling of (a) radicals formed on the carbon atoms in the skeleton of the diol or the diacid, $-\dot{C}R-$, or (b) vinylene groups, $-CH=CH-$, generated in the polymer; whereas the scission reaction β would be expected to occur within the ester moiety, and radicals of two types would result:

$$\underset{\overset{\|}{\text{O}}}{}\underset{\overset{\|}{\text{O}}}{}$$

$$-C-O-CHR- \longrightarrow -CO\cdot + \cdot CHR-$$

$$-C-OCHR- \longrightarrow -C\cdot + \cdot OCHR-$$
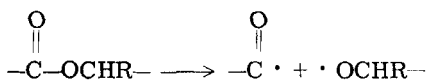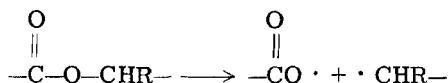
In these studies, an effort was made to determine the location and nature of both the cross-linking and scission reactions.

Straight-Chain Polyesters: Ethylene Glycol Polyesters. In general, the ethylene glycol polyesters were found to undergo moderate degradation with increasing doses up to 100 Mrep (see Tables 4 to 7 and Figs. 1 to 4). The exception of this trend is found in the higher molecular weight polymers of poly(ethylene azelate) and poly(ethylene sebacate) (compare plots B and D in Figs. 3 and 4, respectively). In both these cases there was an initial decrease in intrinsic viscosity at low irradiation doses (indicating a predominance of the scission reaction), which was followed by an increase in intrinsic viscosity with increased radiation. The polymer finally reached the cross-linked gel stage below the 50-Mrep range. This phenomenon of initial degradation followed by final gelation is rather unusual [29-31], and there are only a few instances in which it has been reported [32].

Saito [29-31] has developed a theory that can be used to calculate the changes in intrinsic viscosity when a polymer is subjected to high-energy radiation. This theory was extended by Inokuti [33, 34], who demonstrated that, if the molecular weight distribution is sufficiently broad, the intrinsic viscosity can at first decrease in certain instances, even if it reaches infinity at the gel point. At high extents of reaction in condensation polymers, the weight distribution, as in the case of these polymers where $[\eta] > 0.4$, is very broad [35, 36]. Inokuti [33, 34] concluded that this phenomenon also depends somewhat on the relative importance of the cross-linking and degradation reactions for specific polymers, that is, where the probability of cross-linking of a segment per unit of absorbed radiation is less than four times the probability of degradation in the same segment. It is apparent in the succinates and adipates of ethylene glycol (Figs. 1 and 2) that the probability of degradation is very high and they fail to cross-link. This observation is also true of the lower molecular weight azelate and sebacate esters (Figs. 3 and 4). Since their corresponding high molecular polyesters cross-link, it may be concluded that the α/β ratio has changed by the operation of a "cage effect" [37], a concept which involves the recombination of initial radicals before they can diffuse out of an "active cage" and undergo elsewhere reactions other than recombination. A high intrinsic viscosity would be expected to supply such a "cage" for the glycol polyesters. Yet, it is interesting to note that when poly-(ethylene succinate) of $[\eta] > 0.6$ is irradiated, cross-linking did not occur, even with increasing doses up to 200 megareps. Compared with the azelates and sebacates, the succinates and adipates are more difficult to draw into fibers and, in the solid state, are less crystalline [38, 39], which indicates that crystalline regions act as effective cages. Since the low and high molecular weight polyethylene succinates do not cross-link (whereas the higher esters such as the adipates show an upward slope at 100 Mrep, with a tendency to cross-link, and the azelates and sebacates do cross-link), the effect of the structure of the dicarboxylic in changing the ratio of cross-linking reaction to scission reaction becomes apparent in increasing the cage effect by increasing crystallinity.

This phenomenon does not imply that a viscosity cage effect may not also be simultaneously operative, as may be observed in the low molecular weight azelates and sebacates and in the highly crystalline polyesters such as in the trimethylene, tetramethylene, and pentamethylene diol esters.

Straight-Chain Polyesters: Trimethylene Diol Polyesters. The trimethylene diol polyesters are more resistant to overall degradation than their corresponding ethylene glycol esters, as evidenced in a comparison of Fig. 1 with Fig. 5 for the succinates. Poly(trimethylene succinate) of low molecular weight is not cross-linked on

irradiation (plot A, Fig. 5), which is attributable to a negligible vis-
cosity cage effect. In contrast, its higher molecular polymers
cross-link readily (plots B and C, Fig. 5) as a result of a cage effect
manifested at an intrinsic viscosity of at least about 0.2. The
Inokuti phenomenon is apparent in plot B, Fig. 5. As the number of
methylene groups is increased in the dicarboxylic acid portion of
the trimethylene diol polyesters from the succinates to the adipates
and the sebacates, this minimal value of about 0.2 for the intrinsic
viscosity is maintained. There is not a distinct difference in the
dosage at which gel formation occurs for the poly(trimethylene suc-
cinate) and sebacate, both of which are crystalline polymers; where-
as, for the corresponding glycol esters, wherein the crystallinity in
the succinate is negligible, the dosages at which gel formation oc-
curs are quite different.

   **Straight-Chain Polyesters: Tetramethylene Diol and High Homolo-
gue Polyesters.** Cross-linking is the predominating observable
effect of irradiation on the polyesters of tetramethylene diol, penta-
methylene diol, and decamethylene diol (Figs. 8 to 15), all of which
exhibit the viscosity cage effect; however, they fail to cross-link
below a certain low value of intrinsic viscosity, which is lowest for
poly(decamethylene sebacate), which has 10 methylenes in its diol
and is highly crystalline.

   If the molecular weight is sufficiently high in the saturated linear
polyesters, the segment structure

$$-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}(CH_2)_x\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-O(CH_2)_x-O-$$
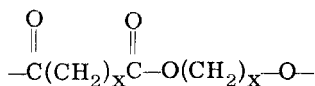
is the primary factor responsible for the direction of the overall radia-
tion reaction. The two reactants which comprise the segment, the
diol and the diacid, do not influence the radiation reaction to the
same extent. Variation of the diol structure has a more noticeable
effect on the direction of the radiation reaction than does the varia-
tion in the diacid. As the number of methylene groups in the diol in-
creases from 2 to 10, the major observable effect of irradiation
changes from degradation to cross-linking. An increase in the
number of methylenes in the diacid has little apparent influence on
the reaction direction. These effects may be interpreted as resulting
from (1) more frequent main chain ruptures occurring in the diol
portion between the ester bonds, particularly, when the segment con-
tains only a few methylene groups, and (2) the prevalence of the
cross-linking reaction within the diacid portion. Stabilization of
the diol ester bonds would be expected to favor the overall effect of
the irradiation reaction toward cross-linking, whereas weakening

of the bonds would favor degradation. The resonance structures of the polyester segments
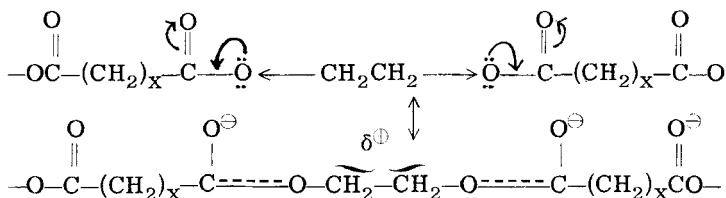
lend some support to this concept.

The electron-withdrawing effect of the carbonyl group pulls on the partially mobile electron of the acyl oxygen, which in turn weakens the C—O and C—C bonds in the diol portion of the segment. Thus, when irradiation ionization or excitation occurs in these partially weakened bonds, a scission occurs. The weakening of these bonds appears to be of sufficient magnitude only where the two ester groups operate through a few methylene groups. This condition is fulfilled in the polyesters of dimethylene diol and to a lesser degree in trimethylene diol polyesters.

The presence of four methylene groups in the diol comer would isolate the electron-withdrawing ester groups sufficiently to make any weakening of main chain bonds ineffective. This decrease in the scission reaction, even if the cross-linking reaction, which appears to occur mainly within the diacid component, is constant, increases the α/β ratio, and, thereby, the cross-linking effect dominates.

It also would be expected that if the diol component is responsible for the scission reaction, a large increase in the number of methylene groups in the diacid would be required before cross-linking occurs easily; whereas, if the diol fragment is stabilized in some fashion, a smaller number of methylene groups would be required to attain the same end effect. These relationships are found in the saturated straight-chain polyesters discussed previously.

Branched Diol Polyesters: Methylethylene Diol Polyesters. Cross-linking was the major effect of irradiation in the branched polyesters studied, which were prepared from 1-methylethylene glycol. Qualitatively, the efficiency of cross-linking was independent of the diacid structure. Gelation occurred at relatively low doses, usually less than 25 Mrep for the polyesters studied, which had initial intrinsic viscosities close to 0.2. This phenomenon indicates the existence of a viscosity cage effect. The behavior of these branched polyesters (Figs. 16 to 19) should be contrasted to the respective linear polyesters based on ethylene glycol (Figs. 1 to 4). The former cross-link, whereas the latter degrade under ionizing

radiation. The following structural formulas illustrate that the two groups differ only by a methyl branch in the diol comer:

$$-CH_2-CH_2-OCO-(CH_2)_x-OCO-$$

Polyesters of ethylene glycol

$$-CH_2-\overset{\overset{\textstyle CH_3}{|}}{CH}-OCO-(CH_2)_x-OCO$$

Polyester of 1-methylethylene glycol
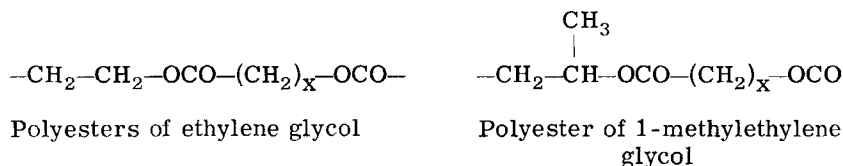
The results shown in Figs. 1 to 4 and 16 to 19 indicate that the introduction of a single methyl group as a branch modifies the α/β ratio so that cross-linking is the favored end result. This result may be due to an increase in the cross-linking reaction by the formation of radicals in the methyl branch, resulting in radical cross-linking due to favorable distance relationships; thus

$$-CH_2-\overset{\overset{\textstyle |}{CH_2}}{\underset{\overset{\textstyle |}{CH_2}}{\overset{\overset{\textstyle |}{CH}}{}}}-OCO-(CH_2)_x-OCO- \Bigg\} \rightarrow -CH_2-\overset{\overset{\textstyle |}{CH_2}}{\underset{\overset{\textstyle |}{CH_2}}{\overset{\overset{\textstyle |}{CH}}{}}}-OCO-(CH_2)_x-OCO-$$
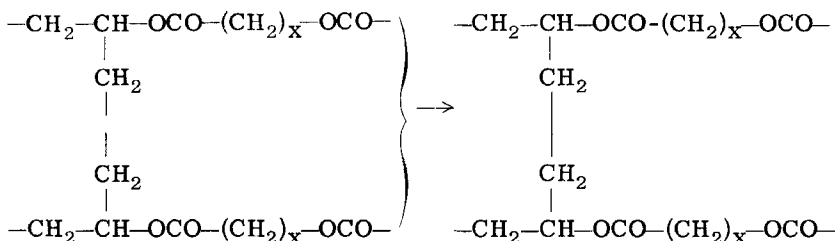
Alternatively, the α/β ratio may be favored by a reduction in the scission reaction occurring in the ester group. Possibly the methyl branch would supply electrons to the partially deficient carbon atom (α to the electron-with drawing ester group) by hydrogen bonding to the partially negative carbonyl oxygen through the formation of a six-membered ring, as shown in the following hyperconjugated structure (for simplicity, the complete segment is not shown):
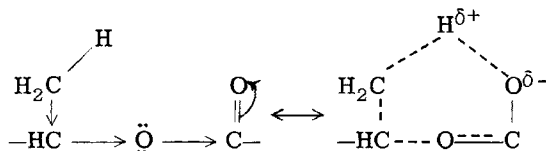
Of the two mechanisms, the radical formation on the branch, which is responsible for the increase in the α/β ratio, is considered to be the least favorable, although it undoubtedly exists to some extent. If radicals are formed on the methyl branches and these radicals are responsible for the increase in the overall cross linking reactions in these polymers, a similar increased effect

should be observable in the polyesters of 2, 2-dimethyltrimethylene diol (Figs. 20 to 23) as compared with the unbranched trimethylene diol esters (Figs. 5 to 7). However, such an effect was not observed.

Similarly, radicals of methyl branches should also be formed and be effective in promoting cross-linking when methyl groups are present in the diacid, whereas the contrary effect, increased scission, is observed in the comparisons of unbranched poly(pentamethylene succinate) (Fig. 11) and poly(pentamethylene adipate) (Fig. 12) with poly(pentamethylene-2-methyl succinate) (Fig. 35). The viscosity cage effect is evident in these 1-methylethylene diol polyesters, but since the methyl substitution greatly reduces the crystallinity of the polymers, none of the polyesters prepared exhibited a crystallinity cage effect.

Branched Diol Polyesters: 2, 2-dimethyltrimethylene Diol Polyesters. The polyesters of 2, 2-dimethyltrimethylene diol crosslink under irradiation and exhibit a viscosity cage effect (Figs. 21 to 23). The location of the methyl groups in the 2 position in the diol excludes the formation of a six-membered ring postulated for the 1-methyldimethylene diol polyesters and, therefore, may be excluded from consideration as a stabilizing factor. The influence of dimethyl substitution in these esters must be considered in a comparison with the unbranched trimethylene diol polymers (Figs. 5 to 7) or with the unbranched pentamethylene diol polyesters (Figs. 11 to 14), which have a total of five carbon atoms in the diol. In general, it may be concluded that little, if any, contribution is made to the cross-linking end result by these methyl groups, and therefore there is minor, if any, production of radicals on the branched methyl groups. In fact, cross-linking is poorer in the poly-(2, 2-dimethyltrimethylene succinate) (Fig. 20) than in the corresponding poly(trimethylene succinate) (Fig. 5), which probably reflects a reduction in the amount of crystallinity, whereas the corresponding adipates (Figs. 6 and 21) and sebacates (Figs. 7 and 23) exhibit the overall cross-linking reaction within the same order of magnitude.

Branched Diol Polyesters: 2, 2-Diethyltrimethylene Diol Polyesters. The 2, 2-diethyltrimethylene diol polyesters were made to determine whether or not an increase in the length of the branches from methyl to ethyl would change their behavior under irradiation. The ethyl branches are located on the carbon-2 atom in the diol and, similarly to the methyl substitution in the same position, could only form seven- or eight-membered rings; thereby, the concept of scission stabilization through the formation of a six-membered ring is excluded. The polyester of the 2, 2-diethyltrimethylene diols (Figs. 24 to 27) cross-links more readily than the corresponding 2, 2-dimethyl derivatives (Figs. 20 to 23), with gelation occurring generally at lower intrinsic viscosities even though the linear disorder is increased and crystallinity thereby decreased. If ring for-

mation is excluded, since this would require the formation of seven-membered rings, the slight increase in the cross-linking reaction may be attributable to bond formation through some function of the ethyl branches; this would require either radical formation or its disproportionation to a pendant vinylidene group, which, in turn, would form cross-links.

Branched Diol Polyesters: 3-Methylpentamethylene Diol Polyesters. In the 3-methylpentamethylene diol polyesters, the methyl branch is on the carbon-3 atoms and thus differs from the previously discussed branched diols whose branches were located on the carbon-1 and carbon-2 atoms. From a comparison of these polyesters (Figs. 28 to 31) with the corresponding pentamethylene diol esters (Figs. 11 to 14), it is observed that the methyl substitution contributes little, if anything, to the cross-linking reaction.

The results for the polyesters considered thus far indicate that the main scission reactions occur in the ester linkages and that the major cross-linking reactions occur in the diacid component in the polyester, whether or not the diol is linear or branched. Therefore, it was interesting to irradiate a number of polyesters derived from branched diacids with both unbranched and branched diols and to observe the effect of irradiation on the intrinsic viscosity of such polymers.

Polyesters of Branched Dicarboxylic Acids. Poly(pentamethylene-2,3-diphenyl succinate). There was no major observable change in the intrinsic viscosity of poly(pentamethylene-2,3-diphenyl succinate) with irradiation (Fig. 32) for samples having initial intrinsic viscosities corresponding closely to those of poly(pentamethylene succinate) (Fig. 11), which cross-linked very readily. In fact, there is slight evidence of degradation in the slope of the curves in Fig. 32. Since no cross-linking occurs, it might be concluded that the hydrogen on the α-carbon atom in the diacid undoubtedly participates in the cross-linking reaction, since the corresponding unsubstituted succinate polyester does cross-link. Such an argument may not be valid, since this failure to cross-link might have been expected because of the benzene ring, which has been shown previously [5] to act as an energy sink and to offer resistance to changes in polymers. It is interesting to note that in these polyesters, the protective nature of the phenyl group is capable of operating through the ester linkages in a fashion similar to the protection to aryl-substituted paraffins over 12 carbon atoms [5].

Polyesters of Branched Dicarboxylic Acids: Poly(pentamethylene-2-methyl succinate). In order to eliminate the energy-sink effect present in diphenyl succinic acid, the corresponding 2-methyl succinate polyester, having the same viscosity ranges (Fig. 35) in which the poly(pentamethylene) succinate cross-links readily, was prepared. No cross-linking was observable in the polymer with an initial intrinsic viscosity of 0.146, and only a slight increase in vis-

cosity was observed for the polymer having an initial intrinsic viscosity of 0.184 after 50 Mrep of irradiation.

This slight change in viscosity may be the result of a molecular weight redistribution brought about by rearrangements resulting from scission-recombination reactions extended over long periods of time. The substitution of the methyl group for hydrogen in succinic acid, which greatly reduces or eliminates cross-linking, indicates that the α-hydrogen in the dicarboxylic acid plays an important role in the cross-linking reaction.

Polyesters of Branched Diols and Branched Diacids. Two polyesters which have branches in both the diol and in the dicarboxylic component of the segmer were prepared. The polymer poly(3-methylpentamethylene-3-methyl adipate) failed to cross-link when irradiated and showed evidence of degradation (Fig. 33), in contrast to poly(3-methylpentamethylene adipate) (Fig. 29), which does cross-link. This behavior indicates that methyl substitution on the β-carbon atom of the dicarboxylic acid retards cross-linking and is similar to the effect of methyl substitution on the α-carbon atom (Fig. 35). The result with poly(3-methylpentamethylene-3-methyl adipate) (Fig. 33) again indicates that methyl substitution in either the diol or the diacid does not contribute substantially to the cross-linking reaction in the positions evaluated in this study. Poly(2,2-dimethyltrimethylene-3,3-dimethyl glutarate) also failed to cross-link readily (Fig. 34), in contrast to the poly(2,2-dimethyltrimethylene adipate) and azelate (Figs. 21 and 22), which cross-link. Again, methyl substitution in the diol does not aid the cross-linking reaction, whereas methyl substitution on the α- or β-carbon atom in the dicarboxylic acid retards cross-linking.

Radiation-Source and Dose-Rate Effect on Saturated Linear Polyesters

Ionization density has been shown to be important in some radiation-induced reactions and unimportant in others [40, 41]. A square-root dependence on the radiation intensity has been shown for free radical polymerizations induced by radiation [41]; however, it has been predicted that the cross-linking of polymers would be independent of radiation intensity [42], and this has been found to be true up to a rate of about 1 Mrep/sec (p. 262 of [43]). In these studies, the polymer poly(tetramethylene sebacate) was selected for study, and the intrinsic viscosity of the irradiated polymers was found to coincide within experimental limits with dose rates from 1 Mrep/hr (about 0.0167 Mrep/min) to 1400 Mrep/min during actual pulses of irradiation (Fig. 36). A similar effect has been shown for polyethylene [44] by determining the amount of insolubles produced on irradiation with a linear accelerator with dose rates within the range 6-2070 Mrad/min, absorbed during actual pulses of irradiation.

In the present studies, the effect was also found to be independent of three radiation sources: a cobalt-60 source, a van de Graaff accelerator, and a linear electron accelerator.

Influence of Air and Film Thickness on Effect of Ionizing Radiation on Intrinsic Viscosity of Poly(tetramethylene sebacate)

The effect of the presence of an oxygen atmosphere on a polymer during its exposure to ionizing radiation tends to cause decomposition in some polymers, whereas in others there appears to be little or no observable effect, and in still others the effect is still a matter of disagreement. Polyethylene, which cross-links readily in the absence of oxygen, reacts with oxygen during irradiation [45]; thus greater dosages are required for gelation [46], and the polymer actually undergoes degradation in the presence of oxygen [47]. Polystyrene, which cross-links at high irradiation dosages in the absence of oxygen, does not gel in its presence, no matter how high the radiation dose [46, 48].

Polyisobutylene does not cross-link at all on irradiation, and the extent of scission is claimed to be about the same whether the irradiation is performed in air, nitrogen, or vacuum [49], although the presence of oxygen changes the nature of the scission products. The presence of oxygen has been claimed to have no influence on the scission of poly(methyl methacrylate) [50], and in another case the scission was claimed to be retarded [51]. Since neither polyisobutylene nor poly(methyl methacrylate) is considered as being cross-linked by irradiation, whether oxygen is present or not, no generalized conclusion can be drawn from their behavior under irradiation. There is no information on the influence of oxygen during irradiation on the saturated linear polyesters of this study and only meager information on poly(ethylene terphthalate), which suffers a decrease in intrinsic viscosity in the absence as well as in the presence of air [14-16].

For oxygen to have a marked effect on the intrinsic viscosity of the polymer, it must, of course, diffuse into the polymer at a rate comparable with the rate of reaction within the polymer. If oxygen diffusion is slow compared with radical formation, all the oxygen initially dissolved in the surface of the polymer will be rapidly consumed, and thereafter the reaction within the polymer will proceed normally as in the absence of oxygen. Thus it has been shown that with thick blocks of polymers, the oxygen effects are confined to the surface, whereas with the films, the effects are observed through the polymer [45, 46, 52].

Both the oxygen-diffusion effect and the thickness effect were observed when poly(tetramethylene sebacate) was irradiated in the presence of oxygen. As the oxygen pressure was increased, more degradation was observed, and, as the film thickness was increased,

degradation was found to decrease (Table 40 and Fig. 37). These observations confirm the work of Charlesby [45] and Dole and his co-workers [52].

Influence of Crystallinity and Orientation on Intrinsic Viscosity of Irradiated Poly(tetramethylene sebacate)

The oriented poly(tetramethylene sebacate) polymer was found to cross-link less readily than the unoriented polymer, which, in turn, cross-linked less readily than the amorphous polymer (Table 41 and Fig. 38). This behavior indicates that cross-linking occurs primarily in the amorphous rather than in the crystalline regions in the polymer, as would be expected if chain motion is restricted in the crystalline regions of the polymer. In this respect, the behavior of these polymers is similar to the behavior of crystalline and amorphous polyethylene under ionizing radiation [53]. In studies of nuclear magnetic resonance, this has been shown to be the case for polyethylene, in which greater resistance to chain motion was indicated in the crystalline regions than in the amorphous regions [54].

For polyethylene it has also been shown [53] that radicals are trapped in the crystalline regions of the polymer and that the more highly crystalline the polymer, the larger the number of trapped radicals. The radicals formed in the crystalline region are not free to move to form intermolecular cross-links because of the restraining forces within the crystal; thus they remain as radicals until they are made to react by one or more of several mechanisms. One method is to react them with oxygen. Another method involves heating the polymer, which causes the development of more cross-links as a delayed reaction. Delayed cross-linking was shown to give fewer cross-links for the same irradiation dose than when the polymer was irradiated in the amorphous state. This decrease is due to the fact that not as many radicals are formed in polymers of high crystallinity, as indicated by evolution of greater quantities of hydrogen when the polymer is irradiated in the amorphous state.

The heating of oriented and unoriented poly(tetramethylene sebacate) polymers, irradiated at their melting points with dosages below gelation, caused an increase in intrinsic viscosity of both polymers. The oriented filament, which is more dense and crystalline than the unoriented filament, had an increase in intrinsic viscosity of 0.026 (from 0.420 to 0.446), whereas the unoriented filament had an increase of only 0.014 (from 0.440 to 0.454). This difference indicates a larger concentration of trapped radicals in the oriented filament than in the unoriented polymer. The final value of the intrinsic viscosity of the oriented filament (after heating) was still less than that of the unoriented filament. The viscosities for both filaments were much less than that for an amorphous polymer.

The viscosities of the crystalline polymers never equaled the intrinsic viscosity of the amorphous polymer when irradiated to the same dose. The behavior of these polyesters parallels, therefore, that reported for crystalline and noncrystalline polyethylenes [53].

When irradiated polyesters are stored in air, a new infrared absorption band appears at 6.42 μ, which is assigned to a

$$\underset{\substack{\| \\ -C-}}{\overset{O}{\|}}\;\underset{\substack{\| \\ -C-}}{\overset{O}{\|}}$$

structure. The appearance of this band indicates the formation of a new carbonyl similar to the formation of carbonyl in polyethylene, which is detected [53] by infrared absorption in the 5.84-μ region.

Changes in Composition of Some Polyesters on Irradiation

When thin films are irradiated, the weight loss of the film due to the loss of the products of the scission reaction is higher than the loss with thicker films (Table 43); thus a diffusion effect is indicated. In thin films the gaseous scission products can diffuse away, whereas in thicker films such fragments may recombine with polymer fragments or with each other and be retained before diffusion can occur. This behavior is indicated by a weight loss of 4.92% for films of 0.25-mm thickness as compared with a weight loss of 1.84% for films of 0.75-mm thickness, after postevacuation to constant weight. Accordingly, films of 0.25-mm thickness were used in studies of the radiation-induced change of the elemental composition of polymers (Table 44) and for the determination of the composition of the gases eliminated from the polymer as a result of scissions during the irradiation (Table 45).

The carbon, hydrogen, and oxygen values for poly(tetramethylene sebacate) were not found to change greatly when irradiated in vacuo, even to large irradiation dosages of 400 Mrep. However, when the polymer is irradiated in air, its oxygen content is greatly increased; thus the percentage of carbon and hydrogen decreases with accompanying changes in the infrared absorption spectra. On the other hand, poly(ethylene succinate) exhibits greater changes in the carbon, hydrogen, and oxygen ratios as a result of a greater number of scissions in it than the poly(tetramethylene sebacate). These changes are also reflected in the gaseous products eliminated from these polymers by irradiation (Table 45). In all the polymers irradiated, the major gaseous product was hydrogen. Qualitatively, this is in agreement with the results from the irradiation of polyethylene, in which case the hydrogen yield has been reported in the range 96-98 mole% [55]. The yield of hydrogen in poly(tetramethylene sebacate) is less than half of that from polyethylene, as a result of the contribution by scissions in the ester links of 16.5 mole% of CO

and 9.7 mole% of CO_2 as well as by other by-products. The yield value of 44 mole% of H is in good agreement with the value of 44.1 reported by Schultz [26] for poly(methyl methacrylate), which had received a dosage of 92 Mrep. Gaseous yields for irradiated poly-(methyl methacrylate) were also reported [26] for CO as 22.8 mole% and for CO_2 as 18.8 mole%; these values are generally of the same order of magnitude as those found for poly(ethylene succinate). The high CO and CO_2 values for poly(methyl methacrylate) would indicate that the rupture of the pendant ester chains occurs more frequently than the rupture of the main chain; thereby the intrinsic viscosity of the polymer is largely unchanged. In poly(ethylene succinate), the ester links are in the primary chain and scissions resulting from irradiation, in the absence of a viscosity or crystallinity cage, would cause a greater loss; this is reflected in the 29.8 mole% loss of products other than H_2, CO, and CO_2, as compared with a total of 7 mole% for poly(methyl methacrylate).

In contrast to poly(ethylene succinate), the composition of gaseous products from poly(tetramethylene sebacate) changes remarkably; the quantity of hydrogen is increased to 49.6 mole%, and the amount of hydrocarbons and other by-products is reduced to approximately 6-7 mole%; this reflects to some degree the activity of a crystallinity cage effect. The increase in hydrogen may also be due to the higher concentration of hydrogen existing in the form of more $-CH_2-$ groups per unit volume of polymer. Poly(decamethylene sebacate), which also is a highly crystalline polymer and has a higher initial concentration of $-CH_2-$ groups per unit volume of polymer, showed not only the viscosity and crystallinity cage effects but also liberated a higher amount of hydrogen (61.9 mole%), about the same amount of RH and other by-products, and a lower total amount of CO and CO_2 (28.4 mole%) than poly(tetramethylene sebacate) (44 mole% of CO plus CO_2). It will also be noted that as the length of the methylene bridges in the polyester increases, not only does the amount of hydrogen formed during irradiation increase, but the mole ratio CO/CO_2 decreases from about 2:1 to 1:1. In this regard, poly(decamethylene sebacate) is very similar to the nonpolymeric cetyl palmitate [27, 28], wherein the mole ratio CO/CO_2 is about 1 and the amount of hydrogen liberated is 85 mole%. However, one may speculate that if more $-CH_2-$ groups are inserted in the decarboxylic acid bridge of poly(decamethylene sebacate), the value of the hydrogen liberated will increase from 62% to values approaching those found in cetyl palmitate and similar compounds.

The irradiation of low molecular weight carboxylic acids caused decarboxylation of the acid among other effects, and the major gaseous product is CO_2, as illustrated by caprylic acid [27, 28], which has a mole ratio CO/CO_2 of about 1:6. In sebacic acid, this

ratio is even more unfavourable, being of the order of 1:35. It is worthy to note that polyesterification with 1, 4-tetramethylene diol reverses this ratio to about 1.5:1, and that when 1, 10-decamethylene glycol is used the ratio becomes approximately 1:1. These results indicate that the major scission reaction in the acid can occur by rupture of the oxygen-hydrogen bond,

$$-CH_2\overset{\overset{\displaystyle O}{\|}}{C}-O-\!\!\!-H$$
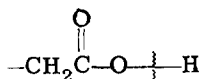
whereafter the hydrogen radical diffuses from the environment and leaves the

$$-CH_2\overset{\overset{\displaystyle O}{\|}}{C}-O\,\cdot$$
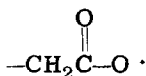
radical to disproportionate and to liberate CO_2. In the case of the polyesters, the radical fragments,

$$-CH_2\overset{\overset{\displaystyle O}{\|}}{C}-O-\!\!\!-CH_2-$$
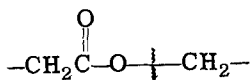
are restrained by a cage effect, and before decarboxylation is completed recombination occurs and the formation of CO_2 is reduced.

The presence of CO may be attributed to (1) a reduction of CO_2 by hydrogen radicals, which would be higher in the polymer than in the nonpolymer because of the possible retention of CO_2 and H in the viscous polymer; or (2) a scission occurring at the carbon-oxygen bond in the acid,

$$-CH_2\overset{\overset{\displaystyle O}{\|}}{C}-\!\!\!-O$$
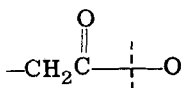
followed by elimination of CO from the

$$-CH_2\overset{\overset{\displaystyle O}{\|}}{C}\,\cdot$$
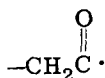
radical. It would be extremely fortuitous in those cases where CO_2 is liberated if exactly one-half of it is reduced to CO; and, for that reason, it is speculated that the presence of equal molar amounts of CO and CO_2 is due to an equal probability of rupture of the car-

bon-oxygen bonds on either side of the oxygen atom derived from the alcohol:

$$\underset{\text{O}}{\overset{\text{O}}{\parallel}}$$

-CH₂C—⦙—O—CH₂—   -CH₂C—O—⦙—CH₂—

(with the carbonyl oxygen shown as:)

$$-CH_2\overset{\displaystyle O}{\overset{\|}{C}}\!-\!\mid\!-O-CH_2- \qquad -CH_2\overset{\displaystyle O}{\overset{\|}{C}}\!-O-\mid\!-CH_2-$$

Grafting of Monomers to Saturated Linear Polyesters

The presence of divinylbenzene admixed with poly(tetramethylene sebacate) or poly(ethylene sebacate) greatly influences the changes in intrinsic viscosity of the resulting grafted polymer even at radiation dosages below the gel point (Table 46 and Fig. 40). This effect indicates a relatively large increase in the cross-linking reaction. When large amounts of divinylbenzene were used, such as 9.09% (commercial divinylbenzene also contains almost an equal amount of ethyl vinylbenzene), the intrinsic viscosity first decreased before it increased eventually to the gel point. This behavior is in accord with the Inokuti effect [33] because of t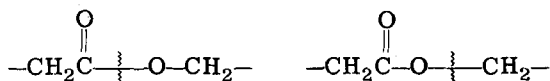he broad molecular distribution resulting from the presence of the polymer and large amounts of monomeric ethyl vinylbenzene and divinylbenzene, which have lower average molecular weights than the polymer.

To confirm that polyfunctional monomers such as divinylbenzene aid cross-linking and thereby reduce the irradiation dosage required to produce gel, the studies were extended to include doses above the gelation dose. The amount of gel formed and the swelling potential of the polymers were determined as a function of both the irradiation dose and the divinylbenzene concentration. The amount of cross-linked polymers formed is proportional to the amount of divinylbenzene present, and the gel increases with irradiation dosages for compositions from 0 to 3.74% divinylbenzene (Table 47 and Fig. 41). With higher amounts of divinylbenzene, such as 9.09 and 33.3% the amount of gel increases very rapidly with irradiation dosages, to a point where a reversal occurs and the amount of gel decreases, which indicates that scissions are occurring. Since such a phenomenon was not observed in compositions with lower amounts of divinylbenzene, it was suspected that the larger amounts of ethyl vinylbenzene present in the mixtures containing 9 and 33% divinylbenzene copolymerized in the graft and during increased irradiation underwent decomposition. There are no published data on alkylated polystyrenes which either justify this conclusion or provide a basis for a comparison. The analysis of Schultz [56] has shown that if the ratio of scission to cross-linking (β/α) is 0.35, then the ratio of the intrinsic viscosity for the irradiated polymer to that for the unirradiated polymer should initially increase and then decrease rapidly. This latter reaction occurs when the ratio R/R^* (where R is a dose below the gelation dose and R^* is the

critical dose for gelation) reaches the range 0. 6-0. 8, which is interpreted as meaning that scissions have occurred and branched polymers have been produced. On the supposition that scission in these polymers was due to ethyl styrene segments, pure p-divinylbenzene (free of ethyl styrene) was used at a concentration of 9% with poly(tetramethylene sebacate) at dosages beyond the point where reversal was encountered with the mixture of divinylbenzene and ethyl vinylbenzene. Under these conditions, the reversal was not encountered up to a dose of 25 Mrep.

To further confirm that the tetrafunctional divinylbenzene monomer is responsible for the increase of the radiation efficiency in cross-linking, a comparison of the cross-linking efficiency of divinylbenzene with that of the difunctional monomer, styrene, was made (Table 48 and Fig. 42). The contrast is remarkable; styrene contributes nothing to the cross-linking efficiency, and, in fact, the amount of gel formed is always less, at comparable radiation dosages, when styrene is present with the polyester. Apparently, most of the styrene appears as grafted branches on a network of cross-linked polyesters, whereas most of the divinylbenzene actually forms bridges between the polyester chains. Accordingly, there is a fundamental difference in the behavior of vinyl monomers of functionality 2 and those of functionality greater than 2 in grafting reaction under the influence of irradiation. The grafting of monovinyl monomers with a functionality of 2 may be properly termed "branch grafting" and that of polyvinyl monomers with a functionality of 4 or more, "bridge grafting." When mixtures of divinylbenzene and poly(tetramethylene sebacate) are irradiated, the divinylbenzene affects the swelling index (Table 50 and Fig. 44), as would be expected from the amount of gel found in the irradiated polymers (Table 46 and Fig. 40); that is, the swelling index decreases with increases in the amount of divinylbenzene and the irradiation dose. However, the low values of approximately 2 and 1 for the swelling index at 9. 09 and 33. 3% divinylbenzene, respectively, fail to reflect the large amount of extractable, soluble un-cross-linked polymer formed in these bridge-grafted polymers when the radiation dose is increased and an inversion occurs (Fig. 41). This same failing is found when measurements of the swelling index of irradiated mixtures of divinylbenzene and poly(ethylene succinate) are compared with the amount of soluble polymer. In these cases, where polymer degradation is encountered simultaneously with the formation of tight, highly cross-linked structures, the swelling index is of limited value and must be evaluated simultaneously with the determination of the amount of gel formed at the same irradiation dose.

As previously discussed, poly(ethylene succinate) did not cross-link at doses up to 200 Mrep. The dosage was extended to 400 Mrep and still gelation was not observed. If multivinyl monomers are in reality bridge-grafting monomers, some evidence to this

effect should be found on irradiation of mixtures of such monomers and polymers which, under identical irradiation doses, do not cross-link. Poly(ethylene succinate) with an intrinsic viscosity of 0.2 is ideally suited for such a test.

This speculation was confirmed, and the amount of gel formed was proportional to the amount of divinylbenzene in the range 1.96-9.09% divinylbenzene (Table 49 and Fig. 43). In the absence of divinylbenzene, no gel was formed even up to a dose of 400 Mrep, and the irradiated polymer remained completely soluble in chloroform. With 1.96% divinylbenzene, gel formation occurs only after a dose of 100 Mrep, and as the amount of divinylbenzene is increased from 1.96 to 9.09%, gel formation occurs at decreasingly lower dosages. An examination of Table 49 shows again that there is no precise relationship between the swelling index (column 4) of the cross-linked polymers and the amount of gel (column 3) in the polymer.

The improvement in irradiation cross-linking efficiency by the use of divinylbenzene with the saturated polyesters of this study is not specific to divinylbenzene but to many multifunctional monomers, such as allyl acrylate, allyl methacrylate, methallyl methacrylate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, diallyl benzene, divinyl phthalate, and many others [57-59]. Nor is the irradiation cross-linking efficiency which results from the use of multifunctional monomers specific only to the type of polyester polymers used in this study. The fact that the irradiation dose at which poly(tetramethylene succinate) (which cross-links readily alone) cross-links can be greatly reduced and that poly(ethylene succinate) (which does not cross-link) can be cross-linked by the use of multifunctional vinyl monomers would indicate that this system might be useful with other polymers. This system should be useful in reducing the dose level of irradiation required to produce the desired degree of cross-linking in those polymers which (1) cross-link readily by radiation alone; (2) cross-link with radiation alone, but because of substantial degradation cross-link with difficulty; and (3) do not cross-link with irradiation or are degraded by irradiation. Polyethylene, polypropylene, and polyisobutylene exemplify these categories, and in all cases the predicted results were obtained [60, 61]. Many other polymers, including polystyrene, the polyalkyl acrylates, the poly(vinyl esters), [60, 61], poly(vinyl chloride) [62], poly(dimethyl silicone), and poly(ethylene terephthalate), are benefited by the presence in the polymer of multifunctional vinyl monomers during irradiation.

An extreme verification of the principle of bridge grafting is its application to substances such as the paraffin waxes, which are usually considered as nonpolymeric. A paraffin wax with a melting point of 60°C is continuously degraded when subjected to irradiation in the absence of air, and no evidence of cross-linking is obtained

up to extreme doses of 2000 Mrep;* yet an infusible, cross-linked bridge-grafted paraffin is obtained when a mixture of 5 parts of divinylbenzene and 95 parts of wax is subjected to a 50-Mrep irradiation dose. A number of natural waxes have also been cross-linked in this manner. Many other types of multifunctional vinyl monomers were also used in irradiation bridge grafting to produce the same results.
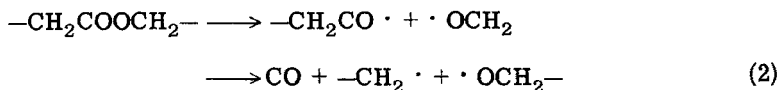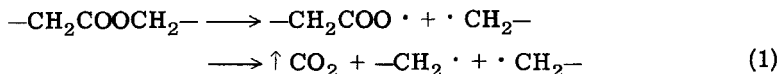
Changes in the Infrared Spectra of Poly(tetramethylene sebacate) on Irradiation

Before irradiation, the main adsorption bands in the infrared are found in the regions 2924, 2865, 1730, 1473, 1456, 1406, 1364, 1348, 1294, 1221, 1176, 1079, 1068, 1053, 965, 857, 672, 730, and 720 cm^{-1}. The changes in the bands in the polymers irradiated in vacuo were, in general, too small at low or medium irradiation dosages to interpret accurately, but the changes when the irradiation was performed in air were very marked.

Minor changes were observed after irradiation in vacuo and in air in the regions 1730, 1176, 1079, and 1068 cm^{-1}, which are characteristic of the ester groups,

$$-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-O-C-,$$
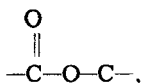
with increasing radiation dose. It was observed that the intensity of an ester band at 1068 cm^{-1} does not change much with irradiation up to 150 Mrep but that it does increase at higher doses of the order of magnitude of 400 Mrep or higher. This low observable change can be explained by the fact that the total decrease in the number of ester groups due to scissions which cause the liberation of CO_2 or CO is small (Tables 44 and 45), and, after irradiation in vacuo, the polymer shows an elemental analysis close to that of the original unirradiated polymer. To explain the loss of CO_2 and CO, the scission can be depicted as occurring in the ester group in the following two ways:

$$-CH_2COOCH_2- \longrightarrow -CH_2COO\cdot + \cdot CH_2-$$
$$\longrightarrow \uparrow CO_2 + -CH_2\cdot + \cdot CH_2- \quad (1)$$

$$-CH_2COOCH_2- \longrightarrow -CH_2CO\cdot + \cdot OCH_2$$
$$\longrightarrow CO + -CH_2\cdot + \cdot OCH_2- \quad (2)$$

*Private communication, J. Olander, High Voltage Engineering, Burlington, Mass.

Recombination of the radicals in Eq. (2) produces an ether linkage, $-CH_2OCH_2-$, which absorbs in the same infrared region. The small total change in the intensity of the 1068-cm^{-1} band is due to the scission [Eq. (1)], wherein the radical fragments recombine to give a hydrocarbon structure $-CH_2CH_2-$. Further irradiation eventually destroys part of the ether linkage, which appears as a further slight decrease in the 1068-cm^{-1} ester band.

The crystallinity of poly(tetramethylene sebacate) decreases with increased irradiation dosages, as indicated by a decrease in the crystallinity bands at 965, 957, 672, and 730 cm^{-1}. The crystallinity band at 730 cm^{-1} decreases more rapidly than the other crystallinity bands.

The intensity of the band at 1406 cm^{-1}, interpreted as due to the methylene group adjacent to the carbonyl group in the acid segment,

$$-CH_2\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-O-$$
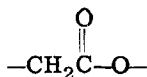
decreases much faster than that of any other band, until about 90% of the total hydrogen is liberated, whereas the bands due to the other $-CH_2-$ groups decrease at a much slower rate. This reaction is a function of irradiation dose both in vacuo and in air, which indicates that the cross-linking reaction occurs primarily through the α-carbon atom of the dicarboxylic acid, and that the β-carbon atom plays a minor role. When the polymer is irradiated in vacuo, no new bands appear in the region 730-1000 cm^{-1}, where any formation of $-CH=CH-$ bonds would be expected to show absorption bands. However, when the polymer is irradiated in air, two new bands are formed, one at 1632 cm^{-1}, which is assignable to the unsaturated structure

$$-C=C-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-$$
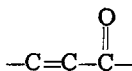
and another at 1558 cm^{-1}, assignable to the structure

$$-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-O-$$
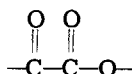
These two bands indicate that the α-carbon atom is most probably the reactive site in the cross-linking reaction and that the β-carbon atom also plays an important but minor role. This observation could explain, in part, the previous finding that methyl group substitution on the α- or β-carbon atom of the dicarboxylic acid retards the cross-linking reaction. A further confirmation of the location of these reactive sites is obtained by the appearance of

the 1632-cm^{-1} band when poly(tetramethylene sebacate), irradiated in vacuo, is allowed to react with air as previously mentioned.

Diagnostic Saponification

The data obtained in the diagnostic saponification of irradiated poly(tetramethylene sebacate) supply some confirmatory evidence that the cross-linking occurs in the dicarboxyl acid component of the segmer. The data obtained by the diagnostic saponification are not completely conclusive; however, since the recovery of the original reactants was not 100%, the small amount of unaccounted diol and diacid could be responsible for a great portion of the cross-linked bonds.

This saponification procedure is difficult to execute to obtain quantitative recovery, and at the present time it has been developed to attain a recovery of the starting reagents of about 99% in the un-cross-linked polymer and of about 98% in the irradiated cross-linked polymers as compared with about 93% when the technique was first tried.

In a comparative study, the cross-linking activity of radicals generated on the α-carbon atoms in dicarboxylic acid was demonstrated by irradiating poly(ethylene succinate) which had been modified with maleic acid and had an intrinsic viscosity of 0.25. This polyester was prepared by reacting 0.9 mole of succinic acid, 0.1 mole of maleic anhydride, and 1.05 mole of ethylene glycol, and by subjecting it to irradiation. Whereas the unmodified poly(ethylene succinate) degraded with increased irradiation dosages (Fig. 1), the maleic-modified polyester gelled at a radiation dose of about 10 Mrep. Similarly, when 0.05 mole of sebacic acid was replaced by 0.05 mole of maleic anhydride in poly(tetramethylene sebacate), the amount of gel at a megarep dose increased from about 15 to 21%.

SUMMARY AND CONCLUSIONS

A number of conclusions may be drawn from the data obtained in these studies on the irradiation of selected saturated straight-chain and branched polyesters. The results show that the structural features of the polyester segment, derived from polyesterification of specific diols and specific diacids, influence greatly the direction and magnitude of the radiation effects.

For the saturated linear polyesters, the diol exerts a strong influence on the direction of the reaction, that is, whether the scission reaction or the cross-linking reaction predominates. In the polyesters of succinic acid, the scission reaction is very evident when the segment is derived from diols having less than three —CH$_2$— groups and thus becomes less as the number of methylene groups is

increased in the higher diols. When the number of methylene groups in the diol is greater than three, an increase in the number of methylene groups in the diacid does not exert a major influence on the cross-linking reaction, but in highly scissionable esters, such as the poly(ethylene esters), an increase in the number of $-CH_2-$ groups in the diacid is required to produce gels. Generally, cross-linking is favored by an increase in the number of methylene groups in the diol through stabilization of the ester link; thus the ester scissions decrease. An increase in the number of methylene groups in both the diol and the acid favors crystallinity in the polymers; this results in a "crystallinity cage" that prevents the migration to some estent of scission fragments and produces a favorable increase in the α/β ratio. An increase in the number of methylene groups in either the diol or the diacid, or in both, results in a greater number of methylene groups per unit volume of segmer, which decreases the probability of an interreaction of the radiation with the scissionable ester link; this reduces the number of probable scissions.

In all cases where the CH_2/COO ratio exceeds 2 : 1, cross-linking is obtained if the intrinsic viscosity, that is, the molecular weight, exceeds a minimum value which is in accord with the Franck-Rabinowitch cage effect. (This behavior is shown as a generalized composite in Fig. 45.)

A generalization of the effect of branches in the polyesters of this study cannot be made, since it depends on the location of the branches in the segment, that is, whether they are located in the diol, in the diacid, or in both.
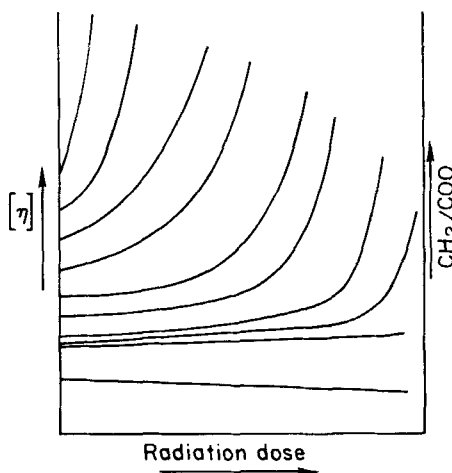

Fig. 45. Generalized effect of irradiation dose on polyesters.

Propylene glycol (1-methylethylene diol) is the simplest branched diol available, and all its polyesters of unbranched linear dicarboxylic acids were found to cross-link with radiation and to exhibit a viscosity cage effect. Cross-linking was evident also in the succinate ester, but this behavior is in marked distinction to that of the corresponding ethylene ester, which does not cross-link. This difference is attributed to a stabilization of the ester linkages by the formation of a hyperconjugated ring structure rather than solely to an increase in the number of carbon atoms; this is apparent when one considers the behavior of poly(trimethylene succinate) or considers the formation of radicals on the branches of such polyesters as 2, 2-dimethyltrimethylene glycol, 2, 2-diethyltrimethylene glycol, and 3-methylpentamethylene glycol. Furthermore, increasing the length of the branch from a methyl group to an ethyl group in the diol did not favor the cross-linking reaction, as would be expected if radical formation occurred readily on the branches.

The introduction of branches on the α-carbon atoms of the diacid sharply retarded cross-linking, as shown by the contrast in the radiation behavior of poly(pentamethylene succinate) with that of both poly(pentamethylene-2-methyl succinate) and poly(pentamethylene-2, 3-diphenyl succinate). In the case of the diphenyl succinate polyester, the energy-sink stabilization effect of aromatic rings was also evident.

Methyl branching on the β-carbon atom of the dicarboxylic acid also reduced the cross-linking reaction, as indicated in the contrast of poly(3-methylpentamethylene adipate) with poly(3-methylpentamethylene-3-methyl adipate) and of poly(2, 2-dimethyltrimethylene adipate) with poly(2, 2-dimethyltrimethylene-3, 3-dimethyl glutarate). In both cases, branches in the alcohol did not increase markedly the cross-linking reaction.

The unusual behavior of certain polyesters, which is reflected by a decrease in intrinsic viscosity at low irradiation doses followed by final gelation at higher doses, confirms the Saito-Inokuti effect, which applies to those cases where the polymer has a broad molecular weight distribution and the probability of cross-linking within the polymer segment is less than four times the probability of degradation. The radiation effects on the polyesters were shown to be independent of the nature of the radiation source and of the dose rates within large limits. The presence of oxygen was shown to exert a degrading effect during irradiation, and thus cross-linking is retarded; this degrading effect is proportional to the oxygen concentration and inversely proportional to the thickness of the polymer, which influences the diffusion of the oxygen into the polymer before its degrading mechanism is effective.

It was concluded also that cross-linking occurs mostly in the amorphous or liquid areas of the polymers, although radicals are generated in the crystalline areas but to a lesser degree. These

group, and, at a slower rate, a second band characteristic of a

$$-C=C-\overset{\overset{\displaystyle O}{\|}}{C}-$$
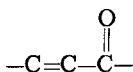
group appeared in the 1632-cm⁻¹ region. No other new bands characteristic of the vinylene group, —CH=CH—, were found to appear in the region 730-1,000 cm⁻¹, where they would be expected to appear. Further evidence indicating that the α-carbon atoms in the dicarboxylic acid are the preferred sites for cross-linking was obtained by saponification of the irradiated cross-linked polymer and isolation of small amounts of multicarboxylic acids.

Vinyl monomers were grafted by irradiation to the polyesters of this study, and a fundamental difference was found in the behavior of monovinyl compounds having a functionality of 2 and multivinyl compounds having a functionality of at least 4. Monovinyl compounds are branched-grafted to the polymers without increasing the amount of cross-linking or lowering the energy requirements of the cross-linking reactions. In contrast, the multivinyl compounds efficiently complement radiation in the production of cross-links in the polyesters and further reduce the dosages required to produce a definite amount of gel. The cross-linking efficiency of the multivinyl compounds is sufficiently great that cross-linked polyethylene succinates can be prepared through their use. The term "bridge grafting" is proposed for this effect and it is not specific to these polyesters alone. Irradiation-produced bridge grafting has broad utility and has been applied to a large number of polymers to (1) reduce the irradiation dosage in those polymers that cross-link readily, (2) cross-link readily those polymers which cross-link with difficulty because of high scission degradation, and (3) cross-link polymers which do not cross-link at all under irradiation or which are highly degraded by irradiation. As an extreme case, irradiation bridge grafting has been extended and shown to be applicable to nonpolymeric systems, such as low-melting paraffin waxes and natural waxes. It was also shown that in some polymers the swelling index is not an accurate measurement of cross-linking values, especially when scission can still occur in segments between the cross-links, and that the determination of the amount of gel is a more suitable method. Studies on the effect of ionizing radiation on other polymers as well as polymers related to the polyesters of this research are still in progress.

REFERENCES

[1]   F. A. Bovey, *The Effects of Ionizing Radiation on Natural and Synthetic High Polymers*, Wiley (Interscience), New York, 1958.

radicals remain trapped in the crystalline areas until released by heating, which results in delayed cross-linking or destruction of the radical by reaction with oxygen.
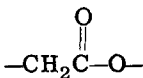
The scission reaction was shown to be located in the ester linkages, and the stability of these linkages was found to be dependent on the nature of the diol. Further confirmation of the site of scission was obtained by an analysis of the gases obtained by irradiation. These gases contained high concentrations of CO_2 and CO, even when irradiated in vacuo.

These yields of CO_2 and CO were compared with the corresponding yields from aliphatic monocarboxylic acids and dicarboxylic acids, from which the major gaseous product of irradiation decomposition is CO_2; thus esterification confers some stabilization to the carboxy group. Polyesterification reverses the CO/CO_2 ratio formed during scission as a result of viscosity and crystallinity cage effects.
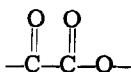
By the introduction of branches on the α and β positions of dicarboxylic acids, it was shown indirectly that the cross-linking reaction occurs by the coupling of radicals formed in these carbon atoms. This concept was confirmed by observing changes in the intensity of the band due to the methylene group adjacent to the carbonyl group in the structure,

$$
\begin{array}{c}
\quad\quad O \\
\quad\quad \| \\
-CH_2-C-O-
\end{array}
$$
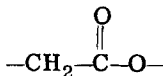
The intensity of this band at 1406 cm^{-1} decreased more rapidly than that of any other band until about 90% of the total amount of hydrogen was liberated; however, the intensity of the bands due to the other methylene groups decreased at a much slower rate. When the polymers were irradiated in air, or when the irradiated polymer was allowed to react with oxygen, one new band appeared at 1558 cm^{-1} by the reaction of oxygen with the

$$
\begin{array}{c}
\quad\quad O \\
\quad\quad \| \\
-CH_2C-O-
\end{array}
$$

group to form the

$$
\begin{array}{c}
O \quad O \\
\| \quad \| \\
-C-C-O-
\end{array}
$$

[2] G. F. D'Alelio and R. Häberli, *Chimia, (Aarau)*, **13**(10), 309 (1959).

[3] A. Charlesby, *Nature*, **171**(4343), 167 (1953).

[4] L. A. Wall, *J. Polymer. Sci.*, **17**(83), 141 (1955).

[5] A. A. Miller, E. J. Lawton, and J. S. Balwit, *J. Polymer Sci.*, **16**(77), 503 (1954).

[6] L. E. St. Pierre and H. A. Dewhurst, *J. Chem. Phys.*, **29**(1), 241 (1958).

[7] M. Dole, Paper 7 of Rept. of Symposium IV, Chemistry and Physics of Radiation Disometry, U.S. Army Chem. Center, Edgewood, Md., Sept. 18-20, 1950.

[8] P. Alexander and A. Charlesby, *Nature*, **173**(4404), 578 (1954).

[9] E. J. Lawton, A. M. Bueche, and J. S. Balwit, *Nature*, **172**(4367), 76 (1953).

[10] O. Sisman and C. D. Bopp, *ORNL-928*, U.S. Atomic Energy Comm., 1951.

[11] C. D. Bopp and O. Sisman, *ORNL-1373*, U.S. Atomic Energy Comm., 1953. (Supplement to *ORNL-928*.)

[12] W. A. Jackson and D. Hale, *Rubber Age*, **77**, 865 (1955).

[13] S. D. Gehman and L. M. Hobbs, *Rubber World*, **130**, 643 (1954).

[14] A. Todd, *Nature*, **174**(4430), 613 (1954).

[15] K. Little, *Nature*, **170**(4338), 1075 (1952).

[16] K. Little, *Nature*, **173**(4406), 680 (1954).

[17] A. Charlesby, V. Wycherley, and T. T. Greenwood, *Proc. Roy. Soc.* (London), **A244**(1236), 54 (1958).

[18] A. R. Schultz and F. A. Bovey, *J. Polymer Sci.*, **22**(102), 485 (1956).

[19] A. Charlesby, *Proc. Roy. Soc. (London)*, **A222**(1148), 60 (1954).

[20] G. F. D'Alelio, *Soc. Plastics Eng. J.*, **8**(3), 25, 40 (1952).

[21] W. H. Carothers and J. A. Arvin, *J. Am. Chem. Soc.*, **51**(8), 2560 (1929).

[22] W. H. Carothers, U.S. Pat., 2, 071, 250 (Feb. 1937).

[23] C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**(5), 880 (1953).

[24] M. Burton, J. A. Ghormley, and C. J. Hochanadel, *Nucleonics*, **13**(10), 74 (1955).

[25] M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1942).

[26] A. R. Schultz, *J. Polymer Sci.*, **35**(129), 369 (1959).

[27] I. A. Breger, *J. Phys. Colloid Chem.*, **52**, 551 (1948).

[28] C. W. Sheppard and W. L. Whitehead, *Bull. Am. Assoc. Petrol Geologists*, **30**, 32 (1946).

[29] O. Saito, *J. Phys. Soc. Japan*, **13**(2), 198 (1958).

[30] O. Saito, *J. Phys. Soc. Japan*, **13**(12), 1451 (1958).

[31] O. Saito, *J. Phys. Soc. Japan*, **13**(12), 1465 (1958).

[32] A. Danno, *J. Phys. Soc. Japan*, **13**(7), 722 (1958).

[33] M. Inokuti, *J. Phys. Soc. Japan*, **14**(1), 79 (1959).

[34] M. Inokuti and K. Katsura, *J. Phys. Soc. Japan*, **14**(10), 1379 (1959).

[35]   P. J. Flory, *J. Am. Chem. Soc.*, **64**, 2205 (1942).

[36]   P. J. Flory, *J. Chem. Phys.*, **12**(11), 425 (1944).

[37]   J. Franck and E. Rabinowitch. *Trans. Faraday Soc.*, **30**, 120 (1934).

[38]   W. H. Carothers and G. L. Dorough, *J. Am. Chem. Soc.*, **52**(2), 711 (1930).

[39]   W. H. Carothers and J. W. Hill, *J. Am. Chem. Soc.*, **54**(4), 1559 (1932).

[40]   R. H. Schuler and A. O. Allen, *J. Am. Chem. Soc.*, **77**, 507 (1955).

[41]   D. S. Ballantine, P. Colombo, A. Glines, and B. Manowitz, *Chem. Eng. Progr. Symp. Ser.*, **11**, 267 (1954).

[42]   C. D. Bopp and O. Sisman, *Nucleonics*, **13**(10), 51 (1955).

[43]   A. Charlesby, *The Effects of Radiation on Materials*, (J. J. Harwood, Henry H. Hausner, J. G. Morse, and W. G. Ranch, eds.), Reinhold, New York, 1958, pp. 261-286.

[44]   G. J. Atchison, *J. Polymer Sci.*, **35**(129), 557 (1959).

[45]   A. Charlesby, *Proc. Roy. Soc. (London)*, **A215**(1121), 187 (1952).

[46]   P. Alexander and D. Toms, *J. Polymer Sci.*, **22**(101), 343 (1956).

[47]   A. Chapiro *J. Chim. Phys.*, **52**, 246 (1955).

[48]   P. Y.-H. Feng and J. W. Kennedy, *J. Am. Chem. Soc.*. **77**, 847 (1955).

[49]   P. Alexander, R. M. Black, and A. Charlesby, *Proc. Roy. Soc. (London)*, **A232**(1188), 31 (1955).

[50]   P. Alexander, A. Charlesby, and M. Ross, *Proc. Roy. Soc. (London)*, **A223**(1154), 392 (1954).

[51]   L. A. Wall and D. W. Brown, *J. Res. Natl. Bur. Std*, **57**(3), 131 (1956).

[52]   M. Dole, C. D. Keeling, and D. G. Rose, *J. Am Chem Soc.*, **76**, 4304 (1954).

[53]   E. J. Lawton, J. S. Balwit, and R. S. Powell, *J. Polymer Sci.*, 32(125), 257 (1958).

[54]   W. P. Slichter and D. W. McCall, *Bull. Am. Phys. Soc.*, **2**(3), 125 (1957).

[55]   M. Dole and C. D. Keeling, *J. Am. Chem. Soc.*, **75**, 6082 (1953).

[56]   A. R. Schultz, P. I. Roth, and G. E. Rathmann, *J. Polymer Sci.*, 22(102), 495 (1956).

[57]   G. F. D'Alelio, U.S. Pat., 3, 075, 904 (Jan. 1963).

[58]   G. F. D'Alelio, U.S. Pat., 3, 074, 866 (Jan. 1963).

[59]   G. F. D'Alelio, U.S. Pat., 3, 082, 161 (Mar. 1963).

[60]   G. F. D'Alelio, U.S. Pat., 3, 003, 310 (Oct. 1961).

[61]   G. F. D'Alelio, U.S. Pat., 3, 071, 923 (Jan. 1963).

[62]   A. A. Miller, *Ind. Eng. Chem.*, **51**, 1271 (1959).