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Crosslinking Efficiencies in the Methyl Methacrylate–Ethylene Dimethacrylate and Ethyl Methacrylate–Ethylene Dimethacrylate Systems. Degradative Analysis by Electron Irradiation

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The intermolecular crosslinking efficiencies, ϵ, of ethylene dimethacrylate have been determined in four methyl methacrylate (MMA)–ethylene dimethacrylate (EDMA) co-polymers and four ethyl methacrylate (EMA)–EDMA copolymers. Random scission of the copolymer networks by 1000 kvp. electrons was employed to determine the number of crosslinked units per gram. MMA–EDMA copolymers having EDMA mole fractions, $\bar{N}_2$, of 0.00578, 0.00291, 0.00147 and 0.000868 exhibited ϵ-values of 0.39, 0.395, 0.44 and 0.48, respectively. EMA–EDMA copolymers with $\bar{N}_2$ of 0.00675, 0.00333, 0.00172 and 0.00102 had ϵ-values of 0.32, 0.36, 0.38 and 0.39, respectively. The extrapolated efficiencies lim ϵ ($\bar{N}_2 \rightarrow 0$) are 0.46 and 0.40. These limiting efficiencies are consistent with the postulate of slightly greater than 50% loss of doubly reacted EDMA units to small intra-chain ring formation. The decrease in ϵ with increase in $\bar{N}_2$ in this low EDMA concentration range is in qualitative agreement with the limited accessibility concept of Loshaek and Fox for pendant double bond isolation on a polymer network.

Introduction

Attempts have been made to determine the crosslinking efficiency of ethylene dimethacrylate (EDMA) in MMA–EDMA copolymerization by dilatometric[1] and by kinetic-incipient gelation[2] techniques. The former method was based on total volume contraction measurements and was a measure of residual unreacted double bonds in the high conversion copolymers. The latter study combined kinetic, viscometric and dilatometric data to examine the classical theory[3,4] of network formation. Correlation of the critical conversion for incipient gelation with polymerization rate and with dimethacrylate concentration permitted estimation of the productive (inter-chain) crosslink formation.

The present paper describes the application of another technique for studying tetrafunctional crosslinking efficiency which is complementary, and in some respects preferable, to the above methods. In recent years the theory of polymer networks[3,4] has been amplified and specialized to treat random crosslinking and degradation of polymers by ionizing radiations.[5] Certain types of polymers, including polymethylmethacrylate[6-8] and polyethyl methacrylate,[9] undergo random main-chain scission without concurrent crosslinking when irradiated. Simple relationships between gel content and radiation dose therefore are available for calculating the number of crosslinked units per gram of MMA–EDMA and EMA–EDMA copolymers. This degradative analysis gives information concerning the final productive crosslinking efficiency of EDMA in the high conversion copolymers and is less sensitive to experimental and theoretical difficulties encountered in handling pregelation and incipient gelation of a polymerizing system.

Experimental

Materials and Polymerization.—The methyl methacrylate (Rohm and Haas) and ethyl methacrylate (Monomer–Polymer) monomers were washed successively with 5% $NaNO_2$, 5% $NaHSO_3$, 5% NaOH and water. The monomers were then dried over $MgSO_4$. Two per cent. by weight of phenyl-β-naphthylamine (PBNA) was added to each and the monomers were distilled through a short Vigreux column. The central cuts used for polymerization were: methyl methacrylate, b.p. 46° at 100 mm.; ethyl methacrylate, b.p. 59° at 100 mm., saponification equiv. 114, C 63.1, H 8.9. Three per cent. by weight of PBNA was added to ethylene dimethacrylate (Monomer–Polymer) and a 73% central cut was obtained by distillation through a Vigreux column at about 1 mm. pressure. No accurate boiling point was obtained due to considerable pressure fluctuation during distillation. The benzoyl peroxide ("Lucidol," Novadel-Agene Corp.) used as a polymerization initiator was not subjected to purification. A mold-release agent Triton X-100 (Rohm and Haas) an aryl alkyl ether alcohol was incorporated in the polymerizing mixtures to facilitate removal of the copolymers from the plate-glass molds, *cf. seq.* Polymerization data indicated no excessive chain-transfer ability for this chemical. Its concentration was held nearly constant in the eight copolymer feeds and no influence upon the measured crosslinking efficiency of EDMA is to be expected.

The feed compositions for the eight copolymerizations are given in Table I. These solutions were syringed into the space between 30 cm. × 30 cm. glass plates separated at the outer edge by a Teflon gasket of 0.68 mm. thickness. The glass plates were taped together around their perimeter with a Scotch brand polyester film tape (#853) having a solvent-resistant adhesive. Polymerization was accomplished in an air oven at 60° for 72 hr. The polymer sheets were then removed from the glass molds and were heated in a 125° oven for 24 hr. Some retardation of the initial polymerization (at 60°) was observed in a zone approximately 1 cm. deep at the upper edge of the polymerizing mixture which was accessible to air through the injection holes. This region was avoided in sampling the polymer sheets for crosslink concentration study. The co-polymer sheets had somewhat uneven surfaces due to differential contraction at higher conversions from the rigidly spaced glass plates. The thickness of the samples used varied in the range 0.65–0.69 mm.

Electron Irradiation and Gel Measurement.—Strips, each weighing approximately 0.15 to 0.20 g., were cut from the copolymer sheets. These were irradiated in air to successive dose levels with 1000 kvp. electrons from a General

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(1) S. Loshaek and T. G. Fox, THIS JOURNAL, **75**, 3544 (1953).

(2) M. Gordon and R.-J. Roe, *J. Polymer Sci.*, **21**, 27 (1956); (b) **21**, 39 (1956); (c) **21**, 57 (1956); (d) **21**, 75 (1956).

(3) P. J. Flory, THIS JOURNAL, **63**, 3083, 3091, 3096 (1941); *J. Phys. Chem.*, **46**, 132 (1942); THIS JOURNAL, **69**, 30, 2893 (1947); "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 347–398.

(4) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943); **12**, 125 (1944).

(5) (a) A. Charlesby, *Proc. Roy. Soc.* (*London*), **215A**, 187 (1952); (b) **222A**, 60, 542 (1954); (c) *J. Polymer Sci.*, **11**, 513 (1953); (d) *Proc. Roy. Soc.* (*London*), **224A**, 120 (1954).

(6) P. Alexander, A. Charlesby and M. Ross, *ibid.*, **223A**, 393 (1954).

(7) L. A. Wall and M. Magat, *J. chim. phys.*, **50**, 308 (1953).

(8) A. R. Shultz, P. I. Roth and G. B. Rathmann, *J. Polymer Sci.*, **22**, 495 (1956).

(9) A. R. Shultz and I. R. Maw, unpublished data.

TABLE I

FEED COMPOSITIONS FOR COPOLYMERIZATIONS (WEIGHT IN GRAMS)

Copolymer MMA–EDMA	MMA	EDMA	X-100	Bz_2O_2
I	92.48	1.0645	0.501	0.1009
II	93.14	.5377	.497	.1002
III	93.47	.2722	.500	.1006
IV	93.56	.1609	.500	.1012
EMA–EDMA	EMA			
I	89.50	1.0556	0.478	0.0994
II	90.86	.5272	.528	.0987
III	90.29	.2701	.500	.1003
IV	90.42	.1603	.499	.1008

Electric Company resonant transformer electron beam generator.[10] All portions of each thin sample received essentially equal (±5%) radiation doses. The electron beam was calibrated against an air ionization chamber furnished by the General Electric Company for absolute intensity determination. The maximum dose rate received by the samples at the beam center was 5.84 megarep min.$^{-1}$. Extensive relative intensity distribution studies were performed to give accurate integral dose calculation for samples transported through the beam on a water-cooled aluminum tray. A value of 1 megarep = 5.24 × 10^{19} electron volts g.$^{-1}$ (in standard air) was used in subsequent calculations. It is possible that a higher value (5.8 × 10^{19} e.v. g.$^{-1}$ megarep^{-1}) is preferable for energy dissipation in a polymer. However, the important consideration is that the same conversion factor is used here as in the linear polymethyl methacrylate degradation study[8] upon which the degradation energy absorption, 59 e.v. per main-chain scission, is based. Addition of 0.5 weight % of Triton X-100 to linear polymethylmethacrylate had no measurable effect on this energy per scission value. The energy absorption per main-chain scission is found to be 75 e.v. for linear polyethyl methacrylate.[9]

The irradiated films were weighed into 100-mesh monel screen cages and immersed in benzene. The extraction of solubles was accomplished by constant gentle stirring of the surrounding benzene for 72 hr. at 25°. The benzene-to-dissolved polymer ratio was never less than 4000:1 by weight. The extracted, coherent gels in their respective cages were dried in air followed by vacuum drying at 100° for 72 hr. As will be mentioned later, even this method failed to free the gels completely of benzene, but the small amount of residual solvent did not critically influence the data interpretation. The dried gels were weighed in their cages and the weight fractions of gel in the irradiated films were calculated. Weights on the swollen gels before drying were also obtained to reveal the nature of the gel-swell relationship. These data are incidental to the more conclusive gel content study and will not be included here.

Results and Discussion

Treatment of Data.—Subject to certain assumptions, which are discussed below, the weight fraction, g, of non-extractable material in a tetrafunctionally crosslinked polymer is given by[3–5]

$$1 - g = [1 + (\delta g/2)]^{-2} \qquad (1)$$

where δ is the number of crosslinked units (two crosslinked units equal one crosslink) per weight-average molecule of the primary (linear polymer) distribution.

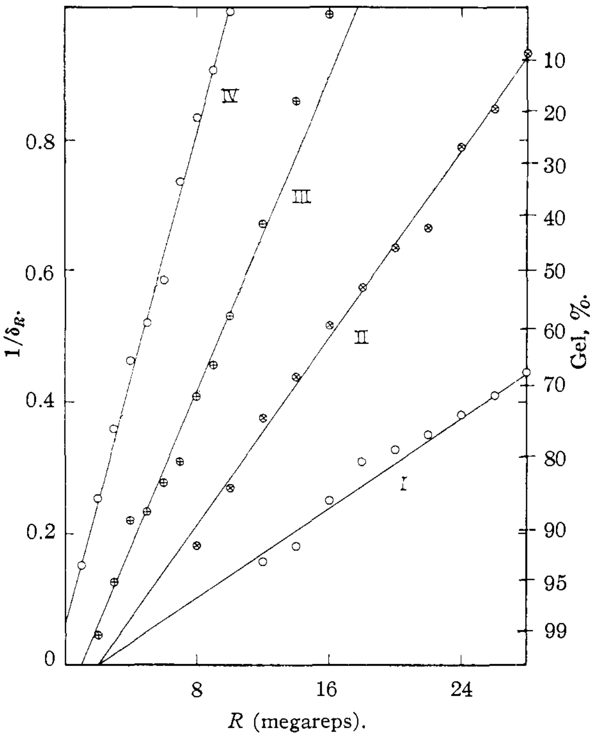

Fig. 1.—Reciprocal of the number of crosslinked units per weight-average primary molecule, $1/\delta_R$, plotted against radiation dose, R, for four MMA-EDMA copolymers. Exterior scale on right indicates per cent. by weight of gel.

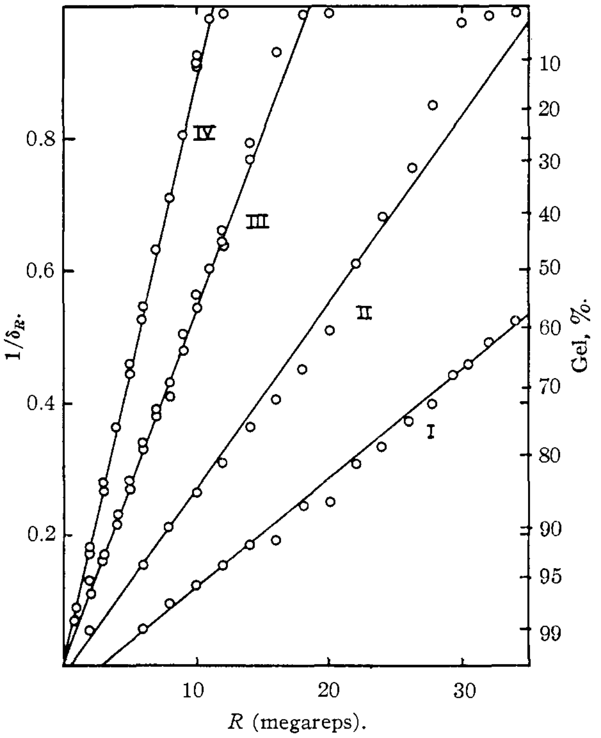

Fig. 2.—$1/\delta_R$ plotted against R for four EMA-EDMA copolymers. Exterior scale on the right indicates per cent. by weight of gel.

If main-chain scissions are introduced at random into the original crosslinked polymer in numbers proportional to R, the radiation energy absorbed per gram of material, the following relation is valid to a good approximation

$$1/\delta_R = 1/\delta_0 + (2AE_d)^{-1}R \qquad (2)$$

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(10) E. E. Charlton and W. F. Westendorp, *Gen. Elec. Rev.*, **44**, 652 (1941); E. J. Lawton, W. D. Bellamy, R. E. Hungate, M. P. Bryant and E. Hall, *Tappi*, **34**, No. 12, 113A (1951).

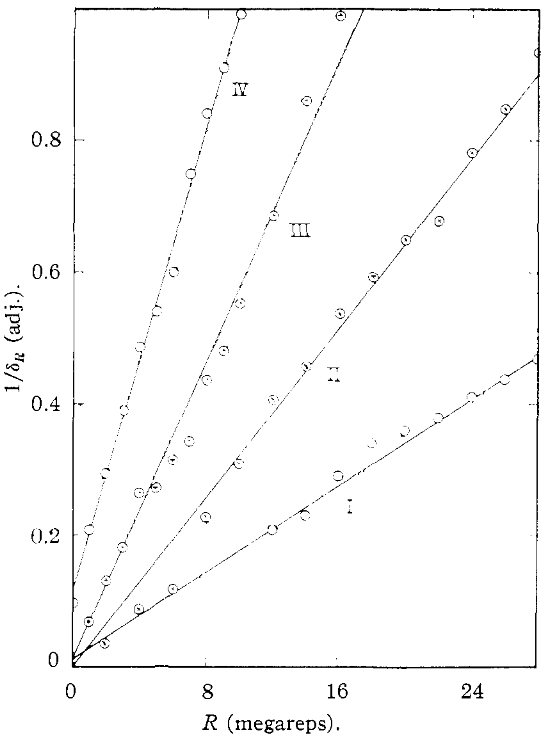

Fig. 3.—$1/\delta_R$ (adjusted) *vs.* R for four MMA–EDMA copolymers; δ_R (adjusted) is calculated by equation 1 assuming g (adjusted) = $0.96g$ (observed).

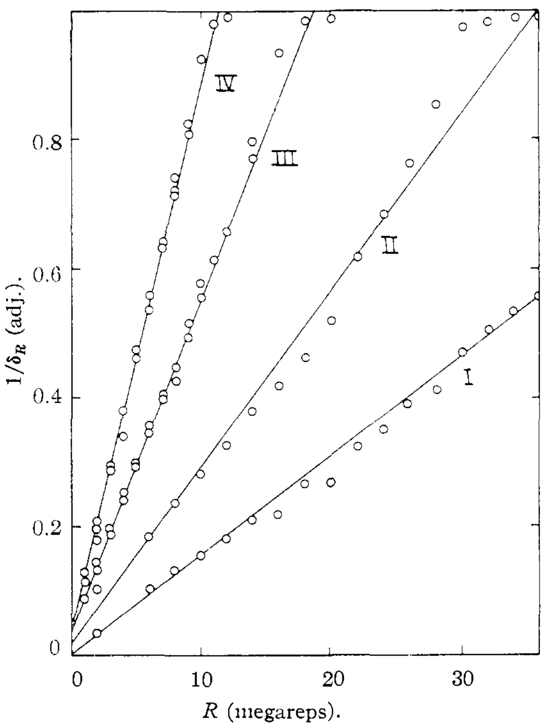

Fig. 4.—$1/\delta_R$ (adjusted) *vs.* R for four EMA–EDMA copolymers; δ_R(adjusted) is calculated by equation 1 assuming g (adjusted) = $0.98g$ (observed).

δ_R is the number of crosslinked units per instantaneous primary weight-average molecule at dose R (e.v. g.$^{-1}$), A is the number of crosslinked units per gram, and E_d (e.v. scission^{-1}) is the total energy dissipation within the polymer per main-chain scission. The three terms in equation 2 obviously represent, respectively, the instantaneous, original and scission-produced number of weight-average primary molecules per crosslinked unit in the polymer.

From the observed g value of each MMA–EDMA and EMA–EDMA copolymer irradiated to dose R, the value of δ_R was calculated by equation 1. The calculated δ_R values are plotted in Figs. 1 and 2 as $1/\delta_R$ against R for the eight copolymers as suggested by equation 2. The corresponding values of g are indicated to the right of the plots. The predicted linear form of the plots is satisfactorily reproduced. However, negative (physically unreal) values for $1/\delta_0$ are found by this direct treatment of the raw gel content data. Some extracted copolymer samples at zero and low radiation dose levels were found to have experimental g values of nearly 1.04 by the described extraction and drying procedure. Preliminary experiments on the effect of extraction time variation indicated no further loss of extractable material over much longer extraction periods. On the other hand, increase of drying temperature or time did slightly reduce the weights of the extracted samples. Rather than employ an extremely elaborate drying procedure, it was decided to apply a reasonable, though arbitrary, correction for incomplete drying. All experimentally observed g values were multiplied by 0.96, *i.e.*, g (adjusted) = $0.96g$ (observed), for the MMA–EDMA series and 0.98 for the EMA–EDMA series. This adjustment made all calculated $1/\delta > 0$. A more exact correction for incomplete drying would introduce a factor nearer unity for the lower g, higher $1/\delta$, samples. A glance at the $1/\delta$ and g scales in Figs. 1 and 2 shows such a refinement to be inconsequential. Figs. 3 and 4 present $1/\delta_R$ (adjusted) plotted against R. Table II gives the intercepts, $1/\delta_0$, and slopes $(2AE_d)^{-1}$ (*cf.* equation 2) for the lines shown in Figs. 1 through 4. It is seen that the slight arbitrary adjustment of the measured gel fractions does not greatly lower the slopes, the quantities of greatest interest. The adjusted intercepts are obviously of no value in estimating the primary chain lengths of the copolymers. Both the relative and absolute magnitudes of the adjusted $1/\delta_0$ for EMA–EDMA II, III and IV are reasonable, however.

TABLE II

SLOPES $(2AE_d)^{-1}$, AND INTERCEPTS, $1/\delta_0$, OF OBSERVED AND ADJUSTED $1/\delta_R$ *vs.* R PLOTS

	Slope (megarep.$^{-1}$)		Intercept (dimensionless)	
MMA–EDMA	Obsd.	Adj.	Obsd.	Adj.
I	0.0170	0.0164	−0.035	0.012
II	.0356	.0322	− .070	.000
III	.0598	.0569	− .060	.012
IV	.0940	.0885	.060	.065
EMA–EDMA				
I	.0168	.0154	− .050	.004
II	.0283	.0275	− .015	.022
III	.0537	.0512	.000	.040
IV	.0887	.0838	.003	.050

E_d, the energy dissipation per main-chain fracture, in poly-MMA undergoing electron irradiation is 59 electron volts[8] and for poly-EMA it is 75 electron volts.[9] Using these E_d and the factor 1 megarep = 5.24×10^{19} e.v. g.$^{-1}$ employed in their calculation the values of A (crosslinked units per gram) for the eight copolymers were obtained from the slopes of Figs. 3 and 4 and are listed in Table III. The maximum theoretical values of A, assuming 100% efficiency of EDMA in useful crosslink formation, were calculated from the feed compositions (Table I). The actual crosslinking efficiencies were then obtained as $\epsilon = A(\text{expt.})/A(\text{max.})$.

TABLE III

CROSSLINKED UNITS PER GRAM, A, AND CROSSLINKING EFFICIENCY, ϵ, FOR EDMA COPOLYMERS

($\overline{N}_2$ = mole fraction EDMA)

Copolymer MMA–EDMA	$\overline{N}_2$	$A \times 10^{-19}$ Max.	$A \times 10^{-19}$ Expt.	ϵ
I	0.00578	6.92	2.70	0.39
II	.00291	3.49	1.38	.395
III	.00147	1.77	0.78	.44
IV	.000868	1.04	0.50	.48
EMA–EDMA				
I	.00675	7.08	2.26	.32
II	.00333	3.51	1.27	.36
III	.00172	1.81	0.68	.38
IV	.00102	1.08	0.42	.39

Theoretical Considerations.—Before discussing these observed crosslinking efficiencies for EDMA a brief examination of the assumptions which are implicit in the data evaluation method employed is in order.

Both equations 1 and 2 rest on the assumption of a "most probable" molecular weight distribution of the primary chains in the copolymer ($\overline{M}_{w0}/\overline{M}_{n0} = 2$). Such a distribution would be produced in a narrow conversion range by radical disproportionation or by chain transfer termination steps in the polymerization. Radical combination produces a slightly "sharper" primary distribution ($\overline{M}_w/\overline{M}_n = 1.5$). A broader than most probable primary molecular weight distribution is actually obtained for the high conversion copolymer due to variation in monomer concentration and in initiation rate throughout the polymerization. Of possibly greater importance is the lengthening of both kinetic and physical primary chains due to decreased radical termination in the crosslinked media at high conversions. The influence of breadth of continuous primary molecular weight distributions upon the g *vs.* δ relation is considerable and must be recognized in handling polymer crosslinking.[5,11] In the present random degradation study, however, deviation of the primary chain-length distribution from the most probable form is eliminated rapidly in the early stages of irradiation. The original distribution loses its identity and the action of further random scission of most probable primary distributions having progressively shorter average chain lengths is the phenomenon measured throughout the major portion of the copolymer degradation. A slight deviation of the lines in Figs. 3 and 4 from linearity would theoretically exist in the region of low $1/\delta_R$ values, but measurement difficulties completely obscure this deviation. The "randomization period" for primary chain length distribution will have a negligible influence on the slope of the observed $1/\delta_R$ *vs.* R plots constructed from data according to equations 1 and 2 when $1/\delta_0$ for the copolymer is small.

Equation 2 is formulated to treat pure random chain scission of a randomly crosslinked network. Crosslink severance is not included in this expression. Assuming equal *a priori* scission probabilities for crosslinks and main-chain bonds, it is easily seen that for random fracture of a net having crosslinks representing only a small fraction of the total units, the crosslink severance contribution to the gel dissolution is minor. Scission of networks having high crosslink concentration or having crosslinks which are extremely labile to the degrading agent must be treated by a more general theoretical formulation. Appendix I presents equations for evaluating such situations. There is no evidence to suggest a markedly greater *a priori* scission probability for the EDMA crosslinks than for the MMA main-chain units under ionizing radiations. The use of equation 2 in treating the data of the present study is consequently readily justified. Appendix II extends the treatment of differing *a priori* scission probabilities to evaluate gel–swell data of randomly scissioned networks. The relations developed give a more quantitative measure of the effects predicted by Horikx.[12] Although these relations are not used in the experimental study at hand their natural derivation from the approach of Appendix I dictates inclusion at this point.

The formulation of equation 2 does not consider intra-chain ring formation occasioned by a radical on a given growing primary chain threading back through one of its own pendant EDMA double bonds. EDMA units engaged in small rings will not contribute to the network as analyzed by electron degradation and will be counted as "wasted" or non-crosslinking units. Concentration considerations will make the occasional fracture of such rings (giving no noticeable network change) unimportant in the present study. EDMA units acting as couplers in large intra-chain rings, on the other hand, will contribute as *bona fide* crosslinks when studied by the random degradation technique. Crosslinking of pendant double bonds on the ring with other primary chains will incorporate the ring into the gel network in such a manner that the network defect created by the ring closure is minor. (In statistically treating the network formation, however, every intra-chain ring closure is unique.) As in the case of deviation of the original primary chain length distribution from most probable, random scission will destroy the identity of large rings in the initial introduction of new chain ends at low radiation doses. A theoretical treatment of the effects of rings of all sizes and in appreciable concentrations on the relation of observed $1/\delta_R$ to R would involve an analysis requiring several assumptions. There is, however, considerable assurance that small rings greatly preponderate[13,14] and their

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(11) A. R. Shultz, Preprint 241, Nuclear Engineering and Science Congress, Cleveland, Ohio, Dec. 1955.

(12) M. M. Horikx, *J. Polymer Sci.*, **19**, 445 (1956).

(13) H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, **18**, 1600 (1950).

(14) R. N. Haward, *J. Polymer Sci.*, **14**, 535 (1954).

effect is that of rendering the involved doubly reacted EDMA units non-contributory to the copolymer network stability.

Discussion

The ϵ (intermolecular crosslinking efficiency) values listed in Table III exhibit a systematic increase with decreasing EDMA concentration in the monomer feed. This is in qualitative agreement with the behavior predicted by Loshaek and Fox[1] who derived explicit expressions relating the ultimate (high conversion) crosslinking efficiencies of dimethacrylates to the dimethacrylate concentration and structure. The principal postulate of their treatment was the existence of a finite accessible domain for each unreacted pendant double bond attached to an existing polymer network. When the concentration of pendant double bonds is reduced by reaction to the extent that domain overlap becomes highly improbable no appreciable further crosslinking occurs. Thus, a certain fraction of pendant double bonds becomes isolated at high conversion; the conditions determining this fraction are the number-average n_c of chain atoms between crosslinked units and the number n_s of chain atoms in the pendant reactive side chain. Assumptions required to couch the theory in a useful mathematical form invalidated its uncritical application to very low initial dimethacrylate feed compositions. In particular the diffusional freedom of crosslinked units about their relative equilibrium positions would enhance crosslinking probabilities in this composition region in a complex manner. The logical extrapolation of the limiting accessibility concept,[1] however, was that as the initial tetrafunctional:difunctional monomer ratio approaches zero ϵ approaches unity.

It was recognized[15] that dilatometric measurement of double bond disappearance does not distinguish between the doubly reacted EDMA units which participate in network crosslinks and those which exist in intrachain rings. Gordon and Roe[2a,d] discuss this problem at some length citing theoretical predictions[13,14] and experimental evidence[16,17] that an appreciable fraction of crosslinkable monomers may be involved in small intrachain rings. This fraction was estimated on approximate steric and rate considerations to be about one-half for EDMA in MMA–EDMA copolymerization (S. Gratch). The present data are plotted as ϵ *vs.* $\bar{N}_2$ (mole fraction of EDMA) in Fig. 5. The empirical straight line through the MMA–EDMA data extrapolates to $\epsilon = 0.46$ and the line drawn through the EMA–EDMA data extrapolates to $\epsilon = 0.40$. The close agreement of the estimated value[15] for lim ϵ ($\bar{N}_2 \rightarrow 0$) with this experimentally measured value must be mainly fortuitous. It is important to emphasize here, however, that lim ϵ ($\bar{N}_2 \rightarrow$ O) as measured by the present random degradative analysis is an accurate indication of the depression of crosslinking due to small ring formation. The ϵ *vs.* $\bar{N}_2$ curves of Fig. 5 do not exhibit the positive curvature predicted by unwarranted extrapolation of the approximate theoretical relationship of Loshaek and Fox[1] into this concentration range. Positive curvature must be found in the region $0.006 < \bar{N}_2 < 0.15$ since a linear extrapolation of the MMA–EDMA line drawn in Fig. 5 would give at $\bar{N}_2 = 0.028$ an ϵ value about one-half the lowest ϵ' value found dilatometrically.[1] The near equivalence of ethylene dimethacrylate's intermolecular crosslinking efficiency in copolymerization with the two similar methacrylates is not surprising. Although there appears to be a systematic separation of the ϵ values obtained for the two systems, the broken line in Fig. 5 passes through the ±10% uncertainty limits in ϵ for all but one copolymer.

The comparison of EDMA crosslinking efficiency as determined by electron degradation of the high-conversion co-polymer with the efficiency as determined by critical conversion for gelation of the copolymerizing system[2d] has several points of interest. The latter method is not concerned with the ultimate crosslinking efficiency. The problem of accessibility for further reaction of pendant double bonds on an established network is nonexistent in the pre-gelation analysis. The critical conversion is dependent on the weight-average primary chain length of the co-polymer (and thereby on the polymerization rate), the tetra-functional monomer concentration, the extent of intra-chain ring formation and the extent of pre-gelation multiple crosslinking of primary chains. Using a few basic assumptions Gordon and Roe examined the classical theory of gelation with regard to the perturbing influence of the latter two factors. They first determined dilatometrically that no acceleration of polymerization attributable to diffusion-controlled radical termination occurred in MMA–EDMA mixtures prior to gelation.[2a] (At least good evidence was presented for the mixtures which reached gelation at low conversion.) The incipient gel point (critical conversion) was measured by observing a fairly abrupt immobilization of a macroscopic probe.[2d] The displacement of gel incipience to higher conversions by increasing the polymerization rate was studied. The modified theory allowed estimation of the intra-chain cyclization from the deviation of the critical conversion *vs.* rate slope from that predicted by ignoring intra-chain cyclization or multiple crosslinking. The experimental data indicated about 67% of the doubly reacted EDMA chain units participated in these latter reactions during the pre-gelation period. Most of these were believed to be accounted for by intra-chain ring formation although experimentally this was indistinguishable from the multiple crosslinking effect. The 67% figure was based upon assumed radical termination by combination. If the terminating step were assumed to be disproportionation, the data would indicate 75% consumption of the EDMA chain units in these side reactions.[18] An attempted theoretical description[2b] of the relative viscosities of the polymerizing mixture suggested the formation of an appreciable number of large intra-chain rings. This viscosity analysis should be largely discounted, however, since it was based upon the erroneous assumption

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(15) S. Loshaek, *J. Polymer Sci.*, **15**, 391 (1955).

(16) W. Simpson, T. Holt and R. J. Zeitie, *ibid.*, **10**, 489 (1953).

(17) M. Gordon, *J. Chem. Phys.*, **22**, 610 (1954).

(18) The author is indebted to Dr. J. C. H. Hwa for detecting an error in the original correction for this effect.

that pre-gelation crosslinking has negligible effect upon the hydrodynamic volume of the polymer molecules. Both theoretical[8,11,19,20] and recent experimental[8,11,21] work show the importance of crosslinking in depressing the molecular volume-to-mass ratio of a polymer system approaching gelation.

The agreement between the kinetic-gel incipience and electron degradation measured intermolecular crosslinking efficiencies for EDMA in the MMA–EDMA system is only fair. The 0.33 or 0.25 value of ϵ observed by the former method might possibly be adjusted to the value lim ϵ ($\bar{N}_2 \rightarrow 0$) = 0.46 if multiple crosslinking were quantitatively accountable. It is not necessary to postulate large intra-chain ring formation to explain the experimental evidence. Small intra-chain rings are shown to exert the limiting influence on ϵ as the initial EDMA concentrations are decreased to very low values. In addition, the electron degradation analysis of the high conversion copolymers reveals the effect of double bond isolation by the existent infinite network.

The analysis of the MMA–EDMA copolymer system by electron irradiation illustrates the potential usefulness of this technique. The greatest limitation is obviously its applicability only to networks which randomly fracture under ionizing radiations. Cured butyl rubber is another system which is amenable to this analysis. Slight concurrent crosslinking during irradiation could be handled theoretically, but accurate knowledge of both scission and crosslinking energies would then be necessary for satisfactory determination of the original crosslink concentration. The crosslinking density range covered in the present study is perhaps optimum for the degradative analysis method. Considerably higher and lower tetrafunctional: difunctional ratio networks could be investigated if desired.

Acknowledgment.—The author wishes to thank Mr. Ivan R. Maw for performing a large portion of the experimental work.

Appendix I

Crosslinking and Scission of a Polymeric Material.—The number of crosslinked units per number-average primary molecule of a polymer is

$$\gamma = q/p \qquad (3)$$

q is the probability that a chosen unit is a crosslinked unit and p is the probability per unit that a chain severance exists. If crosslinks (tetrafunctional), main-chain scissions and crosslink scissions are independently, introduced at random into a material in numbers proportional to an agency R, the crosslinking index may be formulated as

$$\gamma_R = q_R/p_R = [1 - (1 - q_0)e^{-\alpha R}]e^{-2\beta_1 R}/[1 - (1 - p_0)e^{-\beta_2 R}] \qquad (4)$$

q_0 and p_0 are the initial random crosslinking and scission probabilities for an assumed "semi-infinite" progenitor chain before impressment of R. α, β_1 and β_2 are the proportionality constants for crosslinked unit formation, crosslink scission and main-chain scission, respectively, of the polymeric material. As set forth here the crosslinks introduced by R are assumed equivalent to the original crosslinks with regard to subsequent scission. Equation 4 reduces to simplified forms[5] for various limiting values of the parameters.

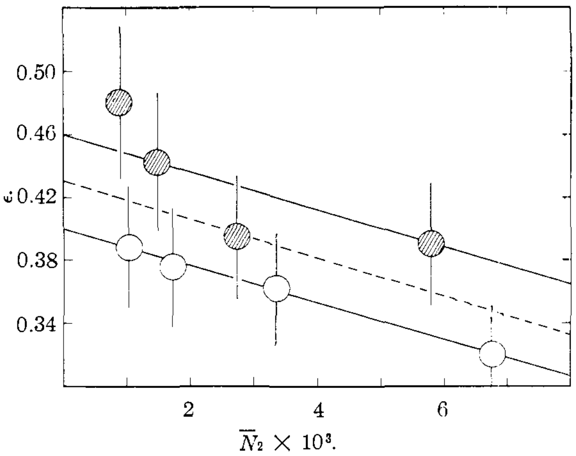

Fig. 5.—Intermolecular crosslinking efficiency, ϵ, *vs.* mole fraction of ethylene dimethacrylate, $\bar{N}_2$, in MMA–EDMA (solid circles) and EMA–EDMA (open circles) copolymers.

Assumed production of the primary linear molecules by random scission of a "semi-infinite" chain makes the primary chain length distribution a most probable one. The number of crosslinked units per weight-average molecule of the initial primary distribution is therefore

$$\delta_0 = 2\gamma_0 = 2q_0/p_0 \qquad (5)$$

The number of crosslinked units per weight-average molecule of the instantaneous primary distribution is

$$\delta_R = 2\gamma_R \qquad (6)$$

since continuance of random scission perpetuates the most probable primary chain length distribution.

Consider R to be the total energy dissipation per gram of polymer undergoing irradiation and assume the absorption to be independent of the extent of reaction. If no crosslinking is induced by the radiation (*i.e.*, $\alpha = 0$) δ_R may be expressed as

$$\delta_R = 2q_0e^{-2\beta_1 R}/[1 - (1 - p_0)e^{-\beta_2 R}] \qquad (6a)$$

Noting that $q_0 = \delta_0\bar{P}_{w0}{}^{-1}$ where $\bar{P}_{w0}$ is the number of units per primary weight-average molecule before irradiation

$$1/\delta_R = (1/\delta_0)e^{2h\beta_2 R}[e^{-\beta_2 R} + {}^1/_2\bar{P}_{w0}(1 - e^{-\beta_2 R})] \qquad (6b)$$

In this equation $h \equiv \beta_1/\beta_2 = E_{d2}/E_{d1}$ is the ratio of *a priori* susceptibilities of crosslinks and main-chain bonds to cleavage by the radiation.

Expanding the exponentials in eq. 6b and substituting $\beta_2 = (\delta_0/\bar{P}_{w0})\ (AE_{d2})^{-1}$ yields

$$1/\delta_R = (1/\delta_0) + [1 + (2B/\bar{P}_{w0})](2AE_{d2})^{-1}R + [2B + 1 + (2B^2/\bar{P}_{w0})](2AE_{d2})^{-2}(\delta_0/\bar{P}_{w0})R^2 + \cdots \qquad (6c)$$

$$B \equiv 2h - 1$$

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[19] B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).

[20] W. H. Stockmayer and M. Fixman, *Ann. N. Y. Acad. Sci.*, **57**, 334 (1953).

[21] A. Charlesby, *J. Polymer Sci.*, **17**, 379 (1955)

Equation 6c reveals more clearly the effect of relative and absolute crosslink and main-chain scission on the $1/\delta_R$ *vs.* R relation. The important factor determining the deviation of initial slope from $(2AE_{d2})^{-1}$ and determining the degree of curvature is the ratio $(2h - 1)/\bar{P}_{w0}$. Figure 6 illustrates the effect of h variation on the $1/\delta_R$ *vs.* R relation as calculated by eq. 6b for $\bar{P}_{w0} = 2000$ and $\delta_0 = 10$. $[1 + (2B/\bar{P}_{w0})]\ (2AE_{d2})^{-1}R$ is chosen for the abcissa scale to give initial coincidence of the curves. For reasonably high $\bar{P}_{w0}$ and moderate δ_0 values there is negligible deviation of the curves from the form of eq. 2 unless h is considerably greater than unity. Discounting a peculiarly high value for h, it is seen readily that eq. 2 is a satisfactory approximation for the copolymers in the present study.

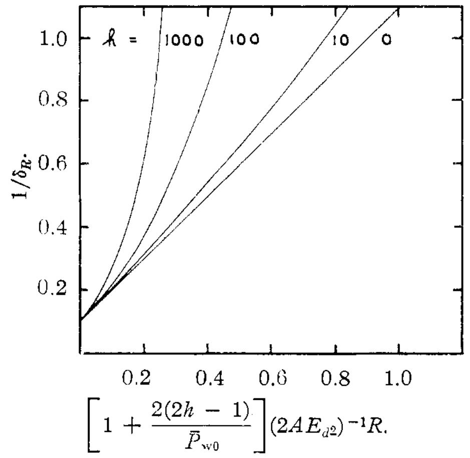

Fig. 6.—Reciprocal of the number of crosslinked units per weight-average primary molecule, $1/\delta_R$, plotted as a function of the original network composition and the absolute and relative crosslink and main-chain scission probabilities. *Cf.* equations 6b and 6c. $\bar{P}_{w0} = 2000$ and $\delta_0 = 10$.

Appendix II

Determination of Relative Stabilities of Crosslinks and Polymer Chains Toward Degradative Agents.—A combination of gel content and swelling data to determine the relative scission rates of crosslinks and main chains of a polymer network was proposed recently by Horikx.[12] This analysis is readily made in theory for the particular type of network and mode of degradation treated above.

The theory of polymer network swelling relates v_2, the volume fraction of polymer in a swollen gel, to the thermodynamic interaction parameter, χ_{12}, and to the number of elastic elements per gram, ν_e, in the gel through[22]

$$\ln (1 - v_2) + v_2 + \chi_{12}v_2^2 + \nu_e d_2 \bar{V}_1(v_2^{1/3} - v_2/2) = 0 \quad (7)$$

d_2 = density of the relaxed polymer network and $\bar{V}_1$ = molar volume of the imbibed solvent. When χ_{12} is known, ν_e may be calculated from swelling data on the gel.

The number of elastic elements per gram in the gel network is given by[12]

$$\nu_e = A[1 - (1 - g)^{1/2}]^2 \quad (8)$$

A as previously defined is the number of crosslinked units per gram in the total polymer (gel plus sol). Therefore in the present formulation

$$\nu_{eR} = [1 - (1 - q_0)e^{-\alpha R}]e^{-2\beta_1 R}[1 - (1 - g_R)^{1/2}]^2 m^{-1} \quad (9)$$

where m is the mass of the polymer unit upon which the probability parameters are based.

Considering only degradation to occur (*i.e.*, $\alpha = 0$) the ratio of the number of elastic elements at irradiation dose R to the number before irradiation is

$$\nu_{eR}/\nu_{e0} = e^{-2\beta_1 R}[1 - (1 - g_R)^{1/2}]^2/[1 - (1 - g_0)^{1/2}]^2 \quad (10)$$

Equations 10, 1 and 6a permit the comparison of weight-fraction sol $(1 - g_R)$, with the swelling variable, $1 - (\nu_{eR}/\nu_{e0})$, as suggested by Horikx. For a crosslinked polymer having given q_0 and p_0 values there is a series of curves relating $(1 - g_R)$ to $1 - (\nu_{eR}/\nu_{e0})$. Each curve corresponds to an $h = \beta_1/\beta_2$ ratio. Figure 7 illustrates the relationship for a polymer having $p_0 = 3.4 \times 10^{-4}$ and $q_0 = 1.36 \times 10^{-2}$ (thus $\delta_0 = 80$) when h = 0, 1, 10, 100 and ∞. The ratio of crosslinks to main-chain units governs the sensitivity of h estimation. Low crosslinking densities render the estimation extremely difficult unless h is large. Possibly the greatest problem is the proper assignment of χ_{12} to the solvent–polymer pair. Also, the assumption of χ_{12} constancy over a large range in v_2 is necessary.

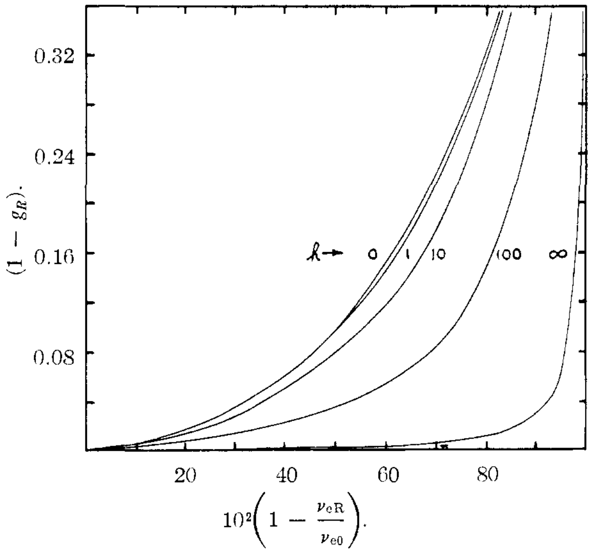

Fig. 7.—Weight fraction extractables, $(1 - g_R)$, plotted against the fractional decrease in elastic elements per gram of gel, $(1 - \nu_{eR}/\nu_{e0})$, for various *a priori* (crosslink scission)/(main-chain scission) probability ratios, h.

This method of estimating relative stabilities of crosslinks and polymer chains deserves further investigation. Careful consideration of the assumed network model and mode of degradation applicability should be made before subjecting a given system to such an analysis.

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[22] P. J. Flory, *J. Chem. Phys.*, **18**, 108 (1950).