

Molecular Weight Changes in Irradiated Polypropylene

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Synopsis

We have shown by two separate measurements that polypropylene when melted after irradiation undergoes crosslinking from the inception of irradiation. The first proof was an immediate increase in the solution viscosity of a narrow molecular weight fraction of polypropylene. The second proof was the marked change in melt-flow properties on irradiation of a broad molecular weight distribution polypropylene. These findings tend to support one of the two currently held views on the action of radiation on polypropylene. In addition we have confirmed previous reports that melting after irradiation contributes to the overall crosslinking reaction.

INTRODUCTION

Earlier investigators showed that the interaction of radiation with polymers usually gave crosslinking, scission, or both.¹ The crosslinking/scission ratio was generally assumed to be independent of dose. With the assumed lack of dependence of the crosslinking/scission ratio on the absolute radiation dose, this ratio could be measured over the most convenient dose range and then the value used for the entire dose range.

Charlesby² and other workers have proposed a number of methods for calculation of this ratio. Essentially this ratio could be determined by assuming an initial molecular weight distribution for the polymer and then measuring the slope of the curve of s or $s + s^{1/2}$ versus $1/r$, where s is the soluble polymer fraction and r is the radiation dose. By this method a crosslinking/scission ratio of about 1.3 was found for polypropylene.

In a recent series of articles, Black and Lyons^{3,4} and then Williams⁵ concluded that, contrary to earlier reports, the crosslinking/scission ratio of a polymer could vary as a function of radiation dose. Specifically they indicated that polypropylene showed this pattern. During the early stages of radiation, the scission reaction was assumed to predominate. Only after the build-up of scission fragments in the system did they find that extensive crosslinking finally occurred. Additional papers describing varying findings have appeared in the literature.⁶⁻¹⁰ However, more recent investigations by Salovey¹¹ on low molecular weight polypropylene indicated that the dominant reaction on irradiation of polypropylene,

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even at low doses, was that of crosslinking. The purpose of our investigation was then to help to resolve these opposing views.

A conclusive experiment that would distinguish between the two mechanisms would consist of the isolation or preparation of a large quantity of a nearly monodisperse fraction of polypropylene and then an exhaustive study of the change in molecular weight and molecular weight distribution of the polymer after irradiation. However the generation of a very narrow molecular weight fraction of polypropylene in such quantities proved difficult.

In the absence of an absolute proof, alternative methods were employed. These were: (1) a comparison of the flow properties of polypropylene irradiated to a series of doses, (2) a determination of the solution viscosities of a narrow molecular weight fraction of polypropylene irradiated at a series of doses, and (3) measurement of the effect of antioxidants or crosslinking inhibitors on the change in solution viscosity of an irradiated standard distribution polypropylene ($\bar{M}_w/\bar{M}_n = 6$).

To avoid changes in irradiated polypropylene prior to measurement of the solution or bulk flow properties, the material was always melted. Melting insured removal of radicals which might contribute to an oxidative degradation of the polypropylene. However with this technique the crosslinking reaction was somewhat enhanced. Without melting of the irradiated polymer consistent results could not be obtained.

The logic behind these experiments is presented in the following section. Although our measurements of the change in physical properties did not quantitatively establish the crosslinking/scission ratio, our experiments appear to prove not only that extensive crosslinking occurs from the inception of irradiation but also that crosslinking is the dominant occurrence.

GENERAL CONSIDERATIONS

As pointed out previously, only direct measurements of molecular weight changes for a well-defined narrow molecular weight fraction of polymer would furnish positive proof of the crosslinking to scission ratio. However the difficulties associated with the isolation of such a large fraction and the required fractionation of the irradiated product made this approach impractical.

Instead we investigated the changes in physical properties on irradiation which show a critical dependence on molecular weight and not on molecular weight distribution. The measurements selected were solution viscosity and bulk viscosity dependence on rate of shear.

Our reasoning for these selections are given below.

Solution Viscosity

For solution viscosity measurements, the reduced specific viscosity RSV can be defined for very dilute solutions by the equation:

$$RSV = K\bar{M}_w^\alpha$$

where K is a constant, \overline{M}_w is the weight-average molecular weight, and α is a constant but having dependence both on molecular weight distribution and on molecular branching. The RSV is determined experimentally by using the equation:

$$\text{RSV} = (\eta - \eta_s)/\eta_s c$$

where η is the viscosity of the solution, η_s is the viscosity of the solvent, and c is the concentration of the polymer in grams per deciliter.

From previous investigations,¹² we know that α is dependent both on molecular weight distribution and also on chain branching. As the breadth of the molecular weight distribution increases, α is known to become smaller. In addition, as the molecule is branched, α becomes smaller.¹³

Narrow Molecular Weight Fraction. Let us assume that a narrow molecular weight fraction of polypropylene in which the distribution is narrower than the most probable distribution, $\overline{M}_w/\overline{M}_n = 2$, is irradiated and that only chain scission occurs. Under these conditions, the distribution will become broader; α will become smaller and the RSV will decrease.

Now if both crosslinking and scission occurred in such a narrow molecular weight fraction with no overall change in molecular weight, α would decrease not only because of the broadening of the distribution but also because of the formation of branched molecules. Either of these factors would result in a reduction of the RSV even in the absence of a molecular weight change. Then, if experimentally the RSV is found to increase on irradiation of a narrow molecular weight fraction of polypropylene, this would be conclusive proof not only of the occurrence of crosslinking but also of the predominance of crosslinking.

Broad Molecular Weight Distribution Polymer. On the other hand, for a broader molecular weight distribution than the most probable, RSV data alone would not serve as a positive proof of the occurrence of crosslinking. A possible method of studying whether crosslinking is occurring from the inception of radiation would be to add a radical trap to the system which would interfere only with crosslinking. If the RSV is greater in the absence of the radical trap than in the presence of this additive, this would be conclusive proof of irradiation crosslinking. However, the absence of such a difference does not prove conclusively that crosslinking is not occurring. This absence may be explained by the additive not acting selectively to reduce the crosslinking.

Bulk Viscosity

The bulk viscosity of a polymer can be used as a diagnostic test for the occurrence of crosslinking. The flow behavior of the bulk polymer has been shown to have a unique pattern which can be reduced to a master curve when one plots η/η_0 versus $\eta_0\dot{\gamma}\alpha_M$, where η is the observed viscosity, η_0 is the zero shear viscosity, $\dot{\gamma}$ is the rate of shear, and α_M is a shift factor.¹⁴

For a polymer undergoing scissioning only, very little variation if any would be expected in the shape of the viscosity versus rate of shear curve. Thus a drastic change in the melt flow pattern would indicate strongly that crosslinking was occurring.

The above considerations were used in our experimental design to show the presence of crosslinking.

EXPERIMENTAL

Materials

For all of our experiments on commercial polypropylene, we used an antioxidant-free sample of polypropylene obtained from Hercules Company and designated as Profax 6501. This material is over 90% isotactic. The added stabilizers in a number of our samples were supplied as follows: 4,4'-thiobis(6-*tert*-butyl-*o*-cresol) from Pittsburgh Consolidated Coal Co., dilauryl thiodipropionate from K and K Laboratories and Ionol (2,6-di-*tert*-butyl-*p*-cresol) from Monsanto Chemical Corp.

Sample Preparation and Irradiation

In systems where additives were used these were blended in the solid phase. The powdered polypropylene, about 2 g., with or without additives, was then sealed in 10-mm. o.d., 8-mm. i.d. glass tubes at pressures of less than 0.3 mm. of Hg. A few samples were melted at this point and then resolidified. These were termed melt-blended samples.

Irradiation was accomplished by passing the samples under the beam of a 2-M.e.v. Van de Graaff electron accelerator at a dose per pass (1) of 0.1 Mrad for the samples with a total dose of 0.1 Mrad; (2) of 0.25 Mrad for the samples irradiated at 0.25, 0.50, and 0.75 Mrad; and (3) of 0.5 Mrad for all samples exposed to 1.0 Mrad or more. The dosimetry and pertinent features of our irradiation facility have been described elsewhere.¹⁵ After irradiation, the samples were heated to 175°C. for just sufficient time to accomplish melting of the polypropylene. This step of melting is required to complete the crosslinking or scissioning and also to eliminate continued free radical reactions in the irradiated polymer. The primary reaction of these trapped radicals based both on a General Electric patent¹⁶ and on our own work presented here is that of crosslinking.

Reduced Specific Viscosity Measurements

Reduced specific viscosities were run in the standard fashion at $135 \pm 0.2^\circ\text{C}$. with 1% of Ionol in the decalin solvent. The reduced specific viscosity in all cases was measured at a polymer concentration of 0.1 g./dl. RSV values on separate samples from the same irradiated master batch could be replicated within 0.03. All samples, except for those in Table I, were measured in duplicate.

Flow Measurements

Flow measurements were obtained by using a capillary extrusion rheometer. Prior to extrusion, additional stabilizers, 0.5% of 4,4'-thiobis(6-*tert*-butyl-*o*-cresol) and 0.5% dilauryl thiodipropionate, were added to the irradiated sample to insure stability of the polypropylene during the extrusion measurements. In addition, solution viscosities of polypropylene were measured both before and after the runs in the extrusion rheometer to determine if any degradation had occurred. Based on the lack of change in the RSV for most samples, no degradation seemed to have occurred. For our flow curves, we used three measurement temperatures, 180, 190, and 200°C. For the capillary, the ratio of the length of the tube to orifice diameter was 30:1.

RESULTS

Solution Viscosity of Irradiated Narrow Molecular Weight Fractions

Samples of four narrow molecular weight fractions of polypropylene were generated by fractionation of Profax 6501.¹⁷ These fractions were irradiated and then analyzed for RSV changes on irradiation. These values are given in Table I. By other means, the \bar{M}_w/\bar{M}_n ratios in these fractions were shown to be less than 2. Although all samples had an \bar{M}_w/\bar{M}_n of less than 2, samples 3 and 4 were of a narrower molecular weight distribution and gave a larger RSV increase on irradiation.

TABLE I
Change in Narrow Molecular Weight Fractions of Polypropylene
as a Function of Dose

Dose, Mrad	RSV, dl./g.			
	Sample 1 ^a	Sample 2 ^a	Sample 3 ^a	Sample 4 ^a
0.0	1.40	2.99	0.93	1.43
0.25	1.41	3.07		
0.50	1.42	2.87		
0.75	1.37	2.67		
1.0	1.25			1.50
3.0				
4.0			1.04	1.60
6.0			0.98	1.50
8.0			1.00	1.46
10.0			0.96	

^a For these series only, RSVs were not determined in replicate because of the limited amount of narrow molecular weight polymer available.

Solution Viscosity of Irradiated Broad Molecular Weight Distribution Polypropylene

Samples of polypropylene containing 0.0, 0.1, 0.2, 0.4, 0.8, and 1.6 parts of stabilizer to 100 parts of polypropylene were irradiated at a series

TABLE II
Reduced Specific Viscosity Changes as a Function of Dose and Additive

Dose, Mrad	RSV, dl./g.			
	None	4,4'-Thiobis- (6- <i>tert</i> -butyl- <i>o</i> - cresol) ^a	Dilauryl thiodi- propionate ^a	Ionol ^a
0.0	3.21 ^b			
0.1	2.71	2.75 ± 0.08 ^b	2.68 ± 0.10 ^b	2.73 ± 0.08 ^b
0.25	2.44	2.55 ± 0.09	2.56 ± 0.06	2.67 ± 0.12
0.50	2.43	2.49 ± 0.10	2.52 ± 0.07	2.48 ± 0.11
0.75	2.11	2.23 ± 0.05	2.19 ± 0.08	2.23 ± 0.07
1.0	1.99	2.08 ± 0.05	2.10 ± 0.04	2.16 ± 0.10
2.0	1.81	1.80 ± 0.06	1.82 ± 0.02	1.84 ± 0.04
3.0	1.51	1.66 ± 0.07	1.72 ± 0.05	1.67 ± 0.04
4.0	1.61	1.61 ± 0.08	1.61 ± 0.05	1.54 ± 0.04
6.0	1.64	1.48 ± 0.08	1.51 ± 0.10	1.46 ± 0.08
15.0	Gel	Gel	Gel	Gel

^a These values are obtained as the average of seven determinations of RSV at 0.1, 0.2, 0.4, 0.8, and 1.6% additive-dry blend and 0.4 and 1.6% melt-blend.

^b RSV at each concentration determined in duplicate.

of doses. Two additional series were run in which the stabilizer instead of being dry blended with the polypropylene was actually melted with the polypropylene to insure distribution on a more microscopic scale. The concentrations of additives in these latter cases were 0.4 and 1.6 parts/100 of polypropylene. In Table II, results are shown both without and with three separate additives. For the three additives, there was very little observable effect on RSV for the entire dose range of 0-6.0 Mrad.

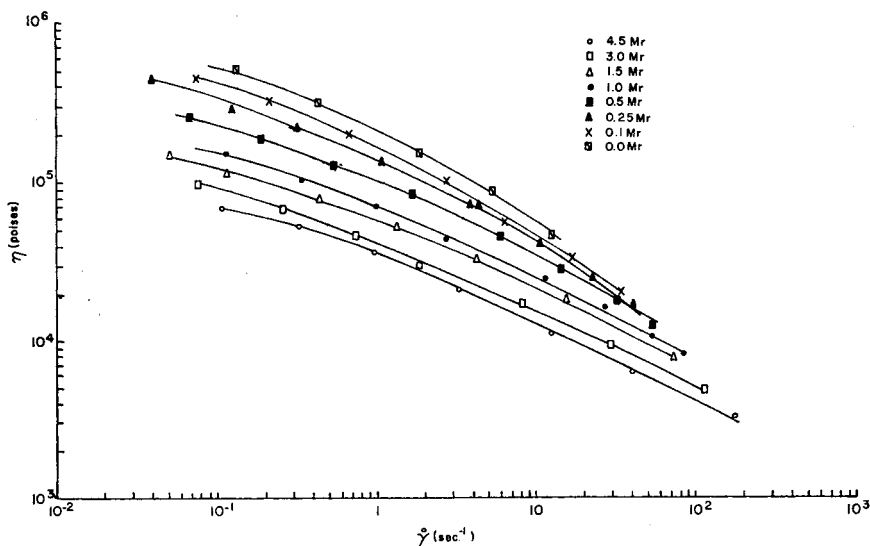


Fig. 1. Flow curves at 180°C.

TABLE III
Reduced Specific Viscosity Changes as a function of
Both Dose and Percentage Additive

Additive, % ^a	Dose, Mrad	RSV, dl./g.		
		4,4'-Thiobis- (6- <i>tert</i> -butyl- <i>o</i> -cresol)	Ionol	Dilauryl thiodipropionate
0.0	6.0	1.64	1.64	1.64
	8.0	1.53	1.52	1.52
	10.0	1.65	1.65	1.65
0.1	6.0		1.47	1.74
	8.0	1.56	1.42	1.60
	10.0	1.51	1.50	1.36
0.2	6.0	1.53	1.48	1.61
	8.0	1.47	1.30	1.58
	10.0	1.35	1.53	
0.4	6.0	1.49		1.54
	8.0	1.28		1.36
	10.0	1.36	1.50	
0.8	6.0	1.54	1.45	1.47
	8.0		1.23	1.48
	10.0	1.10		1.22
1.6	6.0	1.53	1.40	1.34
	8.0	1.28	1.23	1.34
	10.0	0.93	1.19	1.30
0.4 (melt blend)	6.0	1.43	1.39	1.43
	8.0	1.27	1.19	1.43
	10.0	1.26	1.20	1.40
1.6 (melt blend)	6.0	1.35	1.39	1.39
	8.0	1.26	1.23	1.31
	10.0	1.17	1.16	1.34

^a All samples are dry-blended unless otherwise specified.

However, divergencies did occur at higher doses, and are shown in Table III. At the 15.0 Mrad level, all samples regardless of additive, were cross-linked to the point of gelation, indicating very little modification of the crosslinking/scission ratio by the additives.

Bulk Viscosity Measurements of Irradiated Polypropylene Samples

The flow properties of samples of polypropylene, irradiated at the same series of doses as described previously but in the absence of additive, were measured in the extrusion rheometer. Flow curves for these materials at 180, 190, and 200°C. are given in Figures 1-3. In addition, flow curves are also included in these three figures for blends of irradiated and unirradiated polypropylene. For comparison, the master curve of melt viscosity as a function of shear¹⁸ is presented in Figure 4 for unirradiated polypropylene.

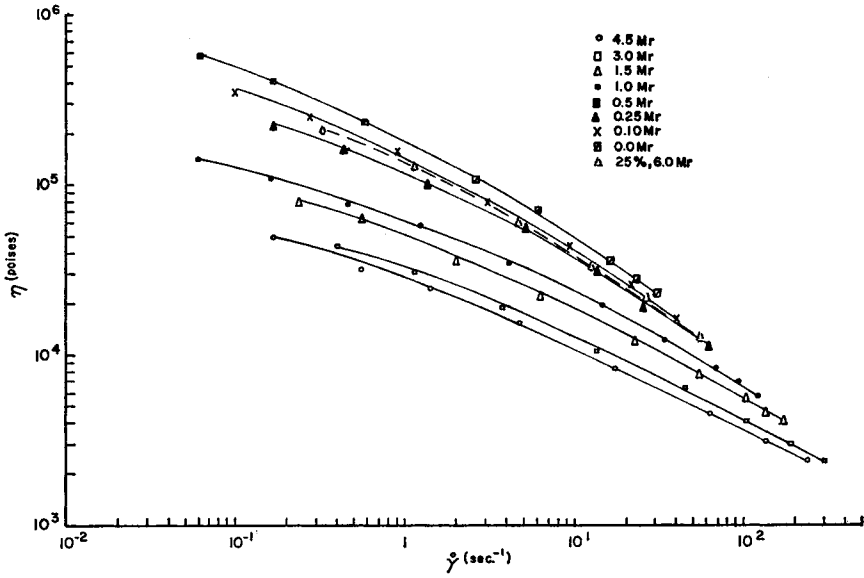


Fig. 2. Flow curves at 190°C.

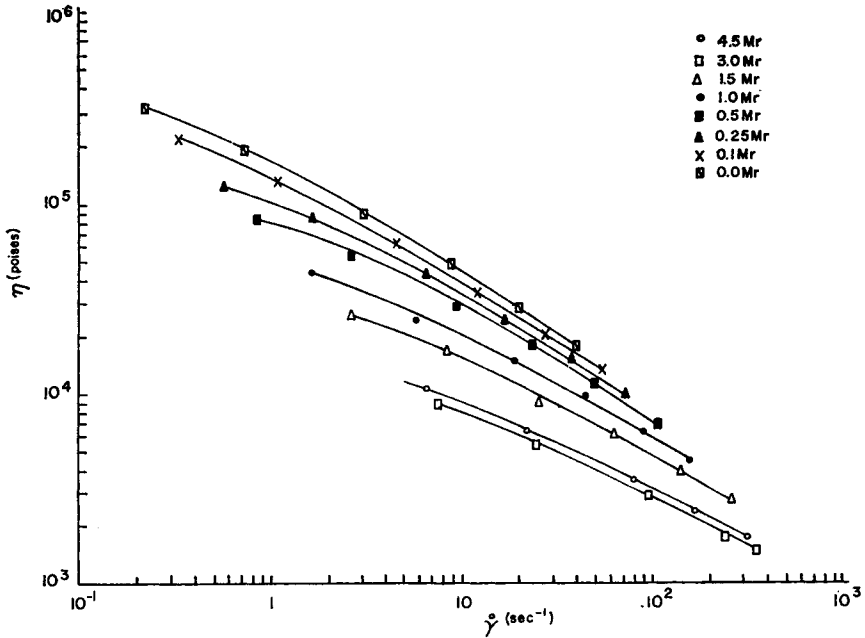


Fig. 3. Flow curves at 200°C.

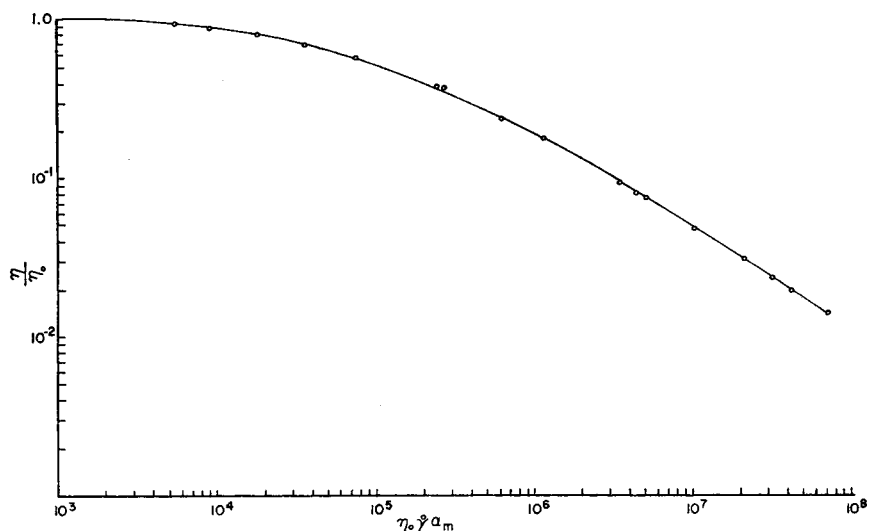


Fig. 4. Master flow curve for polypropylene.

Effect of Melting of Irradiated Samples of Polypropylene on the Crosslinking Efficiency

Some experiments were performed to demonstrate the importance of the melting of polypropylene samples after irradiation. These are presented in Table IV and clearly demonstrate that melting irradiated polypropylene increased the crosslinking in the system.

TABLE IVA
Crosslinking in Pre-gelation Region of Antioxidant-Free Profax 6501

Dose, Mrad	RSV, dl./g.		
	Melted ^a	Immediate solution ^b	Air exposure ^c
0.0	3.83	3.83	3.83
1.5	2.09		
3.0	1.78	1.25	1.04
4.5	1.68	1.07	0.88
6.0	1.67	0.96	0.76

^a Melted samples were heated to 180°C. for 5 min. after irradiation.

^b Samples marked immediate solution were dissolved in decalin after irradiation.

^c Samples marked air exposure were allowed to stand in air for 1 day and then dissolved in decalin.

TABLE IVB
Crosslinking in Post-gelation Region of Antioxidant-Free Profax 6501

Dose Mrad	Sheet-melted ^a		Sheet-air ^b		Powder-melt ^c		Powder-air ^d	
	Xylene- insoluble, %	RSV, dl./g. ^e	Xylene- insoluble, %	RSV, dl./g. ^e	Xylene- insoluble, %	RSV, dl./g. ^e	Xylene- insoluble, %	RSV, dl./g. ^e
1.0	0.0	2.03	0.0	1.80	0.0	2.10	0.0	1.10
3.0	0.0	1.48	0.0	1.47	0.0	1.79	0.0	0.82
5.0	0.0	1.03	0.0	1.21	0.0	1.51	0.0	0.69
10.0	57.0	0.19	5.9		3.8		0.0	0.58
15.0			12.5		11.7		0.0	0.55
20.0	58.8	0.06	25.8		47.4		0.0	0.51
25.0	62.6	0.05	38.6	0.36			0.0	0.59
30.0	64.5	0.02	40.0	0.28	60.6		4.5	0.44
40.0	69.0	0.04	44.5	0.29			22.3	
50.0	70.7	0.05	49.3	0.16	68.5		36.1	

^a Sheet-melted samples were heated to 180°C. immediately after irradiation.

^b Sheet-air samples were allowed to stand for 1 week before the reduced viscosity was determined.

^c Powder-melt were unpressed powder samples that were melted immediately after irradiation.

^d Powder-air samples were unpressed powder samples that were allowed to stand for 1 week before measurement.

^e RSV determined on the xylene-soluble fraction at a concentration of 0.1 g./dl.

DISCUSSION

Analyses of Results Obtained on Narrow Molecular Weight Fractions of Polypropylene

Previously, we have indicated that one method of determining whether crosslinking is occurring simultaneously with chain scission during polymer irradiation is to irradiate a narrow molecular weight fraction of the polymer. The results of such an experiment are shown in Table I. As pointed out under General Considerations, under no circumstances would an RSV increase be found on irradiation unless crosslinking is occurring predominantly during irradiation. As can be seen from Table I, such an increase was found in the very early stages of irradiation for samples 1 and 2 and at the earliest doses used for samples 3 and 4. This increase is then evidence for a crosslinking reaction occurring simultaneously with the known scission in the system. In addition, the results are indirect evidence that the reaction probability of crosslinking to scission may not change greatly in passing from the pre-gelation to the post-gelation region.

Analysis of Results Obtained on Polypropylene-Additive Systems

If we assume that chain scission is intramolecular and that crosslinking is intermolecular, additives that react with polymeric radicals should be more effective in reducing crosslinking than scission. Thus, if polypropyl-

ene is irradiated and then subsequently melted to insure removal of the radicals, there are two possible times when the amount of crosslinking might be reduced by the presence of radical traps. The first is during the irradiation; the second is during the melting of the polymer.

When the additive is incorporated by dry blending, we would not expect any interference with the immediate, irradiation-produced, crosslinking reaction. However, by this technique of admixture, reduction of the melt crosslinking might be expected. On the other hand, when the additive is melt-blended into the system, we might expect both reduction in the immediate, and also in the melt-induced crosslinking.

Now let us examine the results in Table II. First, an initial decline in RSV during irradiation is expected from scissioning a broad molecular weight distribution polymer. This RSV decrease should occur even when crosslinking and chain scission are occurring simultaneously and are equivalent. The reason for this is two-fold; (1) mathematical analysis shows

TABLE V
Change in RSV with Radiation Dose as a Function of Molecular Weight Distribution

Dose, Mrad	RSV, dl./g.		Ratio to initial RSV - (1.00)	
	$\bar{M}_w/\bar{M}_n = 15$ polymer	$\bar{M}_w/\bar{M}_n < 2$ polymer	$\bar{M}_w/\bar{M}_n = 15$ polymer	$\bar{M}_w/\bar{M}_n < 2$ polymer
0.0	2.26	2.41		
0.37	2.32	2.57	0.026	0.066
0.75	2.39	2.81	0.058	0.166
1.12	2.48	3.00	0.097	0.245
1.50	2.57	3.25	0.137	0.348
1.87		3.51		0.456
2.25		3.93		0.631
3.0		5.00		1.075

that intramolecular scissioning is more important in reducing the weight-average molecular weight \bar{M}_w of a broad molecular weight polymer than equivalent crosslinking is in increasing intermolecularly the \bar{M}_w and (2) chain branching derived from crosslinking has been found to modify the solvent interaction constants in the Mark-Houwink equation to give a smaller RSV for crosslinked than for linear material of equal molecular weight.¹³

The importance of the molecular weight distribution on radiation-induced RSV changes was shown as follows. For high density polyethylene, previous investigators have demonstrated that irradiation gave very little chain scission and a predominance of crosslinking.^{19,20} Two samples of high-density polyethylene were examined for changes in RSV as a function of dose. The first sample was a broad molecular weight distribution high-density polyethylene having a \bar{M}_w/\bar{M}_n of about 15, and the second sample was a fraction from this same polyethylene with a \bar{M}_w/\bar{M}_n of less than 2.¹⁷ The RSV data as a function of radiation dose is given in Table

V. The ratio of the RSV of the irradiated samples to the initial RSV — (1.00) is given for simplicity of comparison.

On the basis of Table V, the crosslinking/scission ratio cannot be derived readily from a study of changes in RSV as a function of radiation dose for a polymer having a broad molecular weight distribution. As a corollary, the absence of a marked difference in RSV reduction using radical traps does not preclude the occurrence of crosslinking in the early stages of irradiation.

Analysis of Results Obtained from Melt-Flow Measurements

From the curves of melt flow as a function of shear, we can calculate values for zero shear viscosity, Arrhenius activation energies for melt flow, and RSV to zero shear viscosity ratios. Although all of these determinations are of value in assessing whether a crosslinking reaction is occurring during the early stages of irradiation, a more significant measurement is available. This measurement is a comparison of the response of the polypropylene melt flow to changing shear for both the irradiated sample and the unirradiated sample. For irradiated samples, the standard double logarithmic curve can no longer be superposed into one master curve. Instead, with increasing dose the absolute value of the slope at high rates of shear becomes smaller until at 4.5 Mrad the flow curve can be superposed on the master curve for linear polyethylene.

The change in response appears to be proof of a change in molecular architecture, probably by crosslinking. At all three temperatures this change can be seen at dose levels as low as 0.25 Mrad (Figs. 1–3). An alternative explanation for this dramatic change in response to shear variation would be that of a narrowing of molecular weight distribution.^{21–25} However, when we couple this change in response to shear with the previously found increase in RSV on irradiation of a narrow molecular weight fraction, we conclude that crosslinking is responsible for this dramatic melt flow change.

Some Additional Values Derived from the Melt-Flow Curves

Since the shape of our melt-flow curves has changed as a function of radiation dose, calculations of zero-shear viscosity presented problems. Instead, flow rates at the same rates of shear and at three different temperatures were used to obtain flow activation energies. The results are presented in Table VI.

From the values in Table VI, we note that the activation energy decreases only at the 0.1 Mrad dose and then tends to increase. The decrease at 0.1 Mrad may result from narrowing of the molecular weight distribution by scissioning of the high molecular weight molecules in the system. The increase is expected, since for a branched polymer the flow activation energy at a given temperature is higher than that for a linear polymer of the same chemical structure.

TABLE VI
Flow Ratios for Polypropylene at Various Doses

Dose, Mrad	Flow ratios			Activation energy, kcal./mole	
	190/180°C.	200/190°C.	200/180°C.	200/180°C. ^a	Plotted ^b
0.0	1.28	1.22	1.56	9.5	10.4
0.1	1.20	1.15	1.30	5.6	6.9
0.25	1.35	1.35	1.82	12.8	12.6
0.50	^c	^c	1.75	11.9	^c
1.0	1.45	1.20	1.74	11.8	13.9
1.5	1.52	1.41	2.14	16.2	15.9
3.0	1.55	1.39	2.00	14.8	17.0
4.5	1.55	1.75	2.71	21.2	19.5

^a The activation energy obtained here was calculated only on the basis of the 200/180°C. flow ratio.

^b These values were obtained from the best fit of the three points showing the flow values at 180, 190, and 200°C.

^c The 190°C. sample was lost.

SUMMARY

Two possible mechanisms have been suggested previously for the action of high-energy ionizing radiation on polypropylene. The first indicates that a constant crosslinking to scission reaction occurs in the pre-gelation region and continues into the post-gelation range. The second suggests that the initial process is the scissioning of polypropylene and then, on the build-up of scissioned fragments in the system, crosslinking becomes the dominant occurrence. We have attempted to resolve this conflict by following molecular weight changes in polypropylene by (1) determining changes in reduced specific viscosity of a narrow molecular weight fraction of polypropylene on irradiation, (2) measuring changes in reduced specific viscosity on irradiation of polypropylene both in the absence and presence of free radical traps, and finally (3) examining the flow time of the irradiated polymer as a function of shear in an extrusion rheometer. From these measurements, we have evidence favoring the constant crosslinking to scission mechanism for polypropylene.

We thank the following individuals for their assistance in the experimental phase of this problem: Mr. S. Springer and R. Marcinski for the melt flow measurements, Mr. W. D. Addy for the RSV measurements, Mr. S. Olfky for the irradiations, and Dr. R. Horowitz for supplying the polyethylene and polypropylene fractions.

References

1. E. J. Lawton, J. S. Balwit, and A. M. Bueche, *Nature*, **172**, 76 (1953).
2. A. Charlesby, *J. Polymer Sci.*, **11**, 513 (1953).
3. R. M. Black and B. J. Lyons, *Nature*, **180**, 1346 (1957).
4. R. M. Black and B. J. Lyons, *Proc. Roy. Soc. (London)*, **A253**, 322 (1959).
5. T. F. Williams, *Nature*, **186**, 544 (1960).
6. M. Dole and M. Inokuti, *J. Polymer Sci. A*, **1**, 3289 (1963).

7. M. Dole and W. Schnabel, *J. Phys. Chem.*, **67**, 295 (1963).
8. M. Dole and M. Inokuti, *J. Chem. Phys.*, **38**, 3006 (1963).
9. A. E. Woodward, *J. Polymer Sci. B*, **1**, 621 (1963).
10. B. J. Lyons, *J. Polymer Sci. A*, **3**, 777 (1965).
11. R. Salovey and F. R. Dammont, *J. Polymer Sci. A*, **1**, 2155 (1963).
12. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 308-314.
13. A. Charlesby, *J. Polymer Sci.*, **17**, 379 (1955).
14. L. Zapas, unpublished work.
15. N. S. Marans and W. D. Addy, *J. Appl. Polymer Sci.*, **9**, 3661 (1965).
16. General Electric Co., Brit. Pat. 831,914.
17. R. H. Horowitz, paper presented at 145th Meeting, American Chemical Society, New York, N. Y., September 1963; *Polymer Preprints*, **4**, No. 2, 689 (1963).
18. L. J. Zapas, unpublished work.
19. A. C. Baskett and C. W. Miller, *Nature*, **174**, 364 (1954).
20. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962, pp. 419-420.
21. J. F. Rudd, *J. Polymer Sci.*, **44**, 459 (1960).
22. R. Sabia, *J. Appl. Polymer Sci.*, **1**, 347 (1963).
23. R. Sabia, *J. Appl. Polymer Sci.*, **8**, 1053 (1964).
24. R. Sabia, *J. Appl. Polymer Sci.*, **8**, 1651 (1964).
25. D. E. Grant and S. F. Dieckmann, *J. Appl. Polymer Sci.*, **9**, 3231 (1965).

Résumé

Nous avons montré par deux mesures séparées que le polypropylène par fusion après irradiation subit un pontage suite à l'irradiation. La première preuve était l'accroissement immédiat de la viscosité de la solution d'une fraction de poids moléculaire étroit de polypropylène. La seconde preuve était le changement marqué par les propriétés à l'écoulement à l'état fondu d'un polypropylène irradié de distribution de poids moléculaire large. Ces données tendent à supporter une des vues couramment présentées sur l'action de radiation de polypropylène. En outre, nous avons confirmé nos rapports antérieurs suivant lesquels la fusion après irradiation contribue à la réaction de pontage global.

Zusammenfassung

Durch zwei unabhängige Messungen wurde gezeigt, dass ein nach der Bestrahlung geschmolzenes Polypropylen vom Einsatz der Bestrahlung an vernetzt wird. Der erste Nachweis war ein unmittelbarer Anstieg der Lösungsviskosität einer Polypropylenfraktion mit enger Molekulargewichtsverteilung. Der zweite Nachweis bestand in der deutlichen Änderung der Fließeigenschaften der Schmelze bei Bestrahlung eines Polypropylens mit breiter Molekulargewichtsverteilung. Diese Befunde bilden eine Stütze für die eine der beiden üblicherweise eingenommenen Ansichten über die Einwirkung der Strahlung auf Polypropylen. Ausserdem wurden frühere Befunde bestätigt, dass ein Schmelzen nach der Bestrahlung einen Beitrag zur Gesamtvernetzung liefert.

Received April 22, 1966

Revised August 31, 1966

Prod. No. 1495