

# A Mechanism for the Enhanced Crosslinking of Polyethylene by the Incorporation of Acrylic Acid\*

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The e.s.r. spectrum of acrylic acid, irradiated in the presence of polyethylene at 77 K, differs considerably from that previously found at room temperature. The major components, ascribed to ionic species, are only observed when both acrylic acid and polyethylene are present simultaneously. It is known that under these conditions a sensitized crosslinking occurs, and this is ascribed to a novel ion-radical chain reaction, involving the interaction of the growing poly(acrylic acid) chain end radical with cations formed on the base polyethylene.

It is well established that many monomers may be grafted to polymers by means of high energy irradiation [1]. More recently it has been shown that when acrylic acid is irradiated in the presence of certain polymers (*e.g.* polyolefines) in addition to grafting, the resultant copolymer is crosslinked, and that a high degree of crosslinking may be achieved at doses as low as 0.1 Mrad, well below those needed for conventional crosslinking by a random free radical process. We have attempted to determine the mechanism of this sensitized crosslinking reaction.

The high degree of crosslinking at such low doses points to some form of chain reaction and evidence for this has been obtained from a study using  $^{14}\text{C}$  labelled *n*-hexadecane as a model compound [2]. Acrylic acid polymerizes solely by a free radical mechanism, but it is difficult to imagine any reasonable chain reaction involving only free radicals which could lead to this degree of enhanced crosslinking. Consequently we looked for the possible existence of other reactive species which might be involved in the reaction. In this note we wish to present evidence which indicates that the crosslinking proceeds via a novel ion-radical interaction, quite distinct from the usual radical-induced grafting.

## Experimental

For the mutual grafting experiments approximately 0.5 g samples of low density polyethylene films, Dixopak and Layflat tubing (Transatlantic Plastics) of thickness 0.04 mm, and a high density polyethylene (Metal Box Co) of thickness 0.06 mm, were placed in 10 mm I.D. Pyrex tubing and immersed in excess of solutions of acrylic acid in benzene.

The samples were degassed using the freeze-thaw method and sealed under a vacuum. The tubes were then irradiated at 77 K in the dark or at room temperature at a dose

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rate of 1 Mrad/hour to a total dose of 0.6 Mrads. Following irradiation at 77 K some samples kept at this temperature were exposed to the full spectrum of a Phillips 275 W infrared source about 30 cm distant for 10 minutes, while other samples were allowed to warm to room temperature in the dark. The tubes were then broken open and the polymer samples were thoroughly washed in ethanol to remove homopolymer and dried in a vacuum oven at 60°C. The percentage graft was determined from the weight uptake, and the gel fraction obtained by extraction in boiling xylene [3]. For the samples irradiated at room temperature the grafting solutions also contained about 1% additive as specified below and no care was taken to exclude light.

The e.s.r. samples were prepared in a similar manner except that they were sealed in 5 mm OD Spectrosil tubing. The e.s.r. spectra were recorded on a conventional X-band spectrometer before and after exposure to the Phillips infrared source.

Post-irradiation grafting was carried out by first sealing the polyethylene under a vacuum, irradiating at room temperature to various doses (at 1 Mrad/hour) then introducing the degassed grafting solution *via* a break seal. The sample tubes were allowed to stand for one hour before being broken open for analysis.

## Results and Discussion

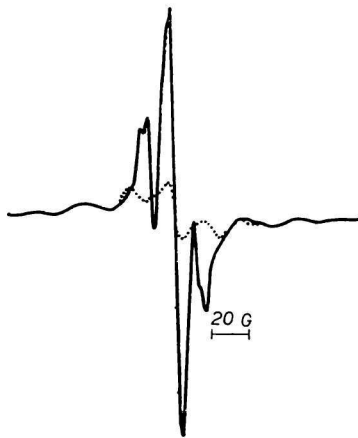
The effect of photobleaching on the yield of graft and gel fraction is given in Table 1. It can be seen that the bleaching produces a marked reduction in both grafting and crosslinking, presumably by the decay of some species involved in both grafting and crosslinking reactions.

The e.s.r. spectra at 77 K consist predominantly of a triplet  $a_H = 14$  gauss with some additional hyperfine structure, and a sharp central singlet. In addition there is a minor contribution from alkyl radicals (Fig. 1). Photolysis at 77 K causes a complete decay of the triplet and singlet components while the alkyl radical spectrum is unaffected. It is important to note that the triplet e.s.r. spectrum is only observed in the presence of both monomer and base polymer and not when the individual components are irradiated

Table 1

Effect of photobleaching at 77 K following gamma-irradiation of polyethylene in acrylic acid/benzene solutions at 77 K

Sample	% Acrylic acid	Dose (Mrads)	Conditions	% Graft	% Gel
Dixopak LDPE	10	0.6	warmed in dark	29	81
	10	0.6	photolyzed	10	39
Layflat tubing LDPE	0.75	0.10	warmed in dark	0.7	19.7
	0.75	0.10	photolyzed	0.4	4
	0.75	0.15	warmed in dark	1.0	22.4
	0.75	0.15	photolyzed	1.17	18.3
	0.75	0.45	warmed in dark	2.3	25.6
	0.75	0.45	photolyzed	0.6	5.7
	0.75	0.6	warmed in dark	1.9	30
	0.75	0.6	photolyzed	0.7	7.7
HDPE	0.75	0.6	warmed in dark	0.8	31.2
	0.75	0.6	photolyzed	0.3	14.8



*Fig. 1.* First derivative e.s.r. spectrum of irradiated polyethylene in 10% acrylic acid/benzene at 77 K.  
 — immediately following irradiation,  
 - - - following bleaching with i.r. lamp.

separately. The intensity of the spectrum is almost unaffected if the acrylic acid concentration is raised over a wide range (1–10% in benzene).

It seems to us reasonable to infer that the decrease in the extent of grafting and crosslinking and the decay of the e.s.r. spectra are related.

The singlet component in the low temperature spectra is most probably due to trapped electrons, and the triplet is thought to be due to some cationic species. This latter assignment is based on experiments using ion scavengers (Table 2). Although the effects are not very large it can be seen that the presence of electron scavengers tends to increase the relative intensity of the triplet spectrum (measured from the outer lines of the triplet) whereas positive ion scavengers produce a slight decrease in intensity.

The effect of charge scavengers on the percentage graft and gel fractions at room temperature is given in Table 3. Again the effects are not very large but the general trend indicates that positive charge scavengers reduce grafting and crosslinking and electron scavengers lead to a slight increase.

We conclude therefore that these graft and crosslinking reactions involve a positive ion which gives rise to the triplet e.s.r. spectrum. Photolysis at 77 K leads to charge neutralization, presumably by detrapping of the electrons, and hence terminates these graft and crosslinking reactions.

*Table 2*

Effect of 1% additives on intensity of triplet spectrum at 77 K obtained from LDPE in 10% AA/benzene irradiated to 0.6 Mrads at 77 K

Additive	Relative intensity of triplet
nil	10
diphenyl (-)	16
<i>p</i> -nitro benzoic acid (-)	18
NH <sub>3</sub> (+)	7
<i>n</i> -butyl vinyl ether (+)	11

(-) electron trap, (+) positive ion trap.

Table 3

Effect of 1% additives on graft and gel for irradiation of LDPE in 10% AA/benzene at room temperature (0.6 Mrads)

Additive	% Graft	% Gel
nil	30	60
diphenyl	34	67
NH <sub>3</sub>	13	45
n-butyl vinyl ether	14	45

We have not as yet definitely identified the species giving the triplet e.s.r. spectrum but we have some evidence which indicates that the ion is associated with  $-\text{CH}_2-$  groups on the polyethylene chain, and not with the acrylic acid. Thus the triplet spectrum is observed when either acrylic acid or methacrylic acid are used in the solution in the presence of polyethylene, nylon 11, or polypropylene, but not when poly(tetrafluoroethylene), and only slightly when 90% deuterated polyethylene are used as base polymers [7].

The spectrum observed following irradiation at room temperature of the acrylic acid solution alone is a broad triplet and is due to propagating chain end acrylic acid radicals [4, 5]. Irradiation of polyethylene itself yields the usual spectra of alkyl and allyl radicals [6]. No evidence of the low temperature triplet spectrum was obtained in either case. A consequence of this is that the sensitized crosslinking reaction (if due to these ionic species) should not occur during post-irradiation grafting at room temperature. Surprisingly it was found that post-irradiation grafting of polyethylene with acrylic acid

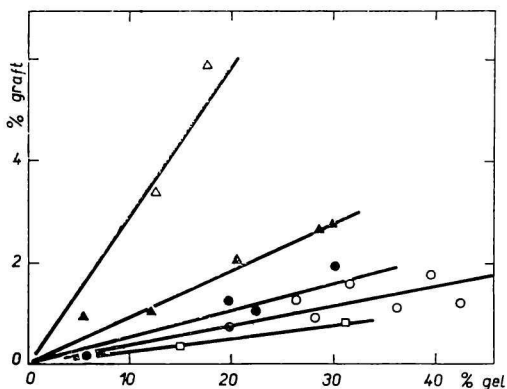


Fig. 2. Variation of % gel and % graft for polyethylene samples grafted under various conditions. Increasing values obtained with increasing dose up to a total of 0.6 Mrads.  $\Delta$  post-irradiation grafting,  $\blacktriangle$  mutual grafting of LDPE with 0.75% AA/benzene at room temperature,  $\bullet$  mutual grafting of LDPE with 0.75% AA/benzene at 77 K,  $\circ$  mutual grafting of HDPE with 0.75% AA/benzene at room temperature,  $\square$  mutual grafting of HDPE with 0.75% AA/benzene at 77 K.

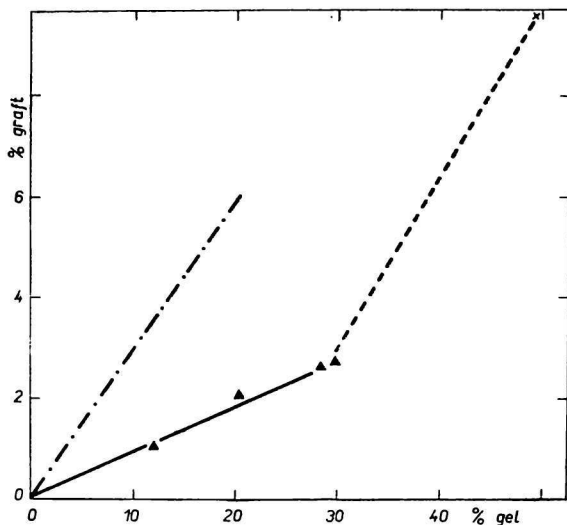


Fig. 3. Variation of gel with graft for LDPE samples at RT.

— · — · — post-irradiation grafting, — mutual grafting up to 0.2 Mrads,  
 - - - - subsequent mutual grafting using fresh solution following pre-irradiation  
 grafting up to 0.15 Mrads.

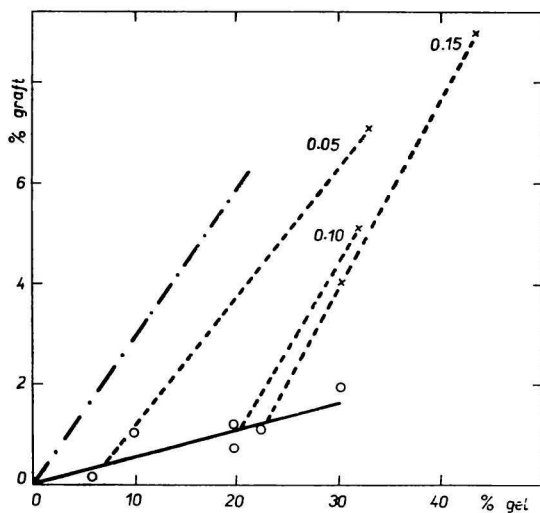


Fig. 4. Variation of gel with graft for LDPE at 77 K.

— · — · — post-irradiation grafting, — mutual grafting at 77 K up to 0.6  
 Mrads, - - - - subsequent mutual grafting following pre-irradiation at 77 K to 0.05, 0.10,  
 0.15 Mrads respectively, with intermediate warming.

does give a gel fraction as measured by xylene extraction, and this seems to preclude the possibility of an ionic mechanism being responsible. However the ratio of % gel to % graft is appreciably lower than that obtained by mutual grafting (Fig. 2).

We therefore considered the possibility of two distinct processes occurring. One is the conventional free radical reaction in which the grafting is initiated by radicals produced by irradiation of the base polymer; this may lead to a very small number of crosslinks due to radical recombination reactions. In addition since the grafted polyacrylic acid chains are not soluble in the non polar xylene, at high graft levels extraction in xylene may give an apparently insoluble fraction which is not a true measure of crosslinking, but rather due to physical entanglements.

The second process is that which involves the ionic intermediate and which is a much more efficient crosslinking reaction. The relatively higher gel fractions at low graft levels and low temperature is indicative of this. We have evidence that this is indeed the case. We had observed that the extent of grafting and crosslinking was apparently limited by the amount of acrylic acid monomer that could diffuse into the polyethylene, and which is itself limited by depletion of acrylic acid in the grafting solution due to homopolymerization. It was thought likely that re-irradiation in a fresh solution might permit one to extend the linear plots out to give much higher gel fractions. Subsequent irradiation however leads to a much lower gel/graft ratio and the curve appears to parallel that obtained from post-irradiation grafting (Fig. 3).

A similar experiment was carried out for samples irradiated at 77 K when homopolymerization is negligible. Following irradiation to 0.05, 0.10, and 0.15 Mrads at 77 K the samples were warmed to room temperature, thus permitting more acrylic acid to diffuse into the polyethylene. Subsequent irradiation at 77 K gives results which again parallel those obtained by post-irradiation grafting (Fig. 4). It appears that the reactions occurring following preliminary grafting are substantially different to the initial grafting reaction.

The e.s.r. spectra of samples irradiated at 77 K show the typical ionic triplet which grows in intensity up to at least 0.6 Mrads. However, pre-irradiation of similar samples to 0.15 Mrads followed by warming to room temperature (to permit some grafting to occur) then recooling to 77 K and re-irradiating to an additional 0.15 Mrads does not give the ionic triplet (Fig. 5).

We conclude therefore that two distinct reactions may occur in polyethylene, irradiated in the presence of acrylic acid. In addition to the conventional grafting reaction an efficient crosslinking reaction occurs which proceeds *via* an ionic mechanism. The production of the ionic intermediate is markedly reduced or even completely eliminated when a certain amount of acrylic acid chains are grafted on to the base polymer. This is confirmed by an e.s.r. study of a polyethylene-acrylic acid copolymer, which shows no ionic component in the e.s.r. spectrum, nor does it crosslink when irradiated at 77 K to these low doses.

It should be pointed out that to obtain consistent results care has to be taken to mini-

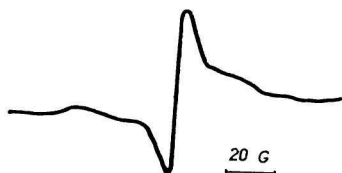


Fig. 5. First derivative e.s.r. spectrum of irradiated polyethylene in 10% AA/benzene following pre-irradiation to 0.15 Mrads and intermediate warming.

mise post-irradiation grafting particularly for samples irradiated to  $> 0.2$  Mrads. Some of the scatter in the results is undoubtedly due to this problem.

We propose a tentative mechanism for the ionic reaction which seems to accommodate the following known facts:

- i) Acrylic acid polymerizes by a free radical mechanism.
- ii) An ionic intermediate is involved in the crosslinking reaction, and the ion appears to be associated with the polyethylene chain.
- iii) The crosslinking proceeds *via* a chain reaction mechanism.
- iv) Acrylic acid is known to form hydrogen bonded dimers [8].
- v) The e.s.r. spectrum found with polyethylene + acrylic acid is different from that seen in high or low density polyethylene alone irradiated under similar conditions. It is also different from the copolymer.

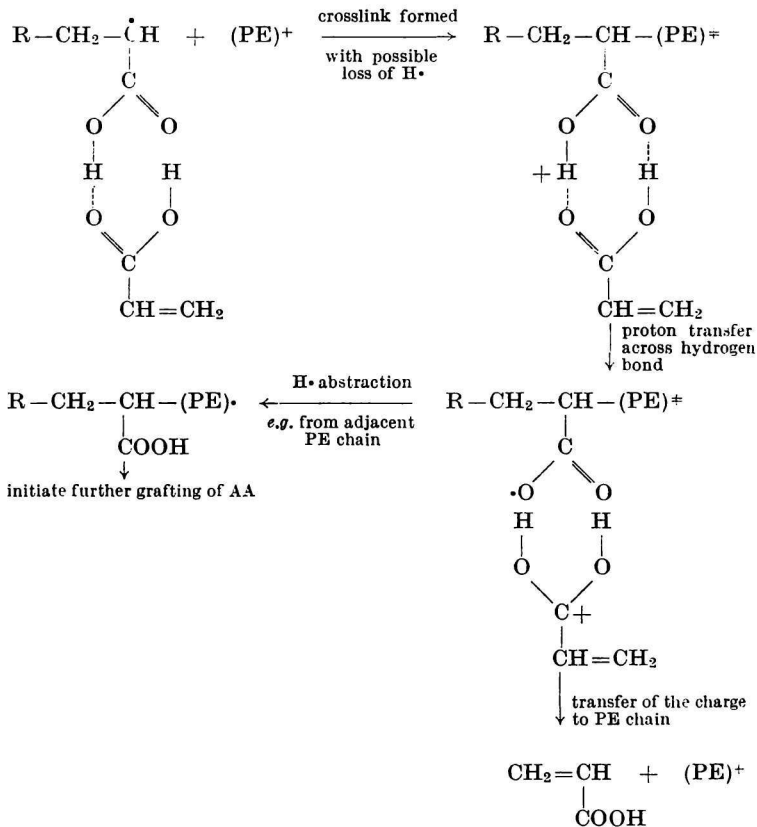
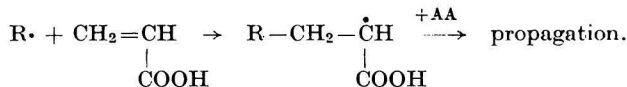


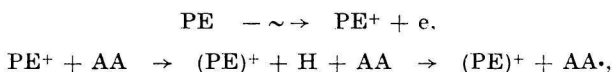
Chart 1

Proposed reaction scheme for enhanced crosslinking of polyethylene by the incorporation of acrylic acid.

The initiation of the grafting reaction presumably occurs at radical sites on the polyethylene



Several tentative reaction schemes may be envisaged for the crosslinking reaction, involving an ionic reaction and proton transfer across hydrogen bonds. One of them is shown in Chart 1.  $(\text{PE})^+$  and  $(\text{PE})^\cdot$  are not precisely defined here, and the latter may be a polyethylene radical. To obtain the link between acrylic acid and polyethylene a hydrogen atom must be released from the polyethylene chain. This may be envisaged in the formation of  $(\text{PE})^\cdot$  which from e.s.r. data differs from  $\text{PE}^\cdot$  (in the absence of acrylic acid). Thus we may postulate the following initial reactions



where the latter can graft or polymerize. The subsequent reaction of  $(\text{PE})^+$  with  $\text{AA}\cdot$  is shown in the figure, and leads to the formation of further  $\text{PE}^+$  to continue the chain reaction. A further reaction involving H abstraction also leads to the formation of radical copolymer.

The net result of such a reaction scheme would be the formation of a crosslink, the initiation of a second growing chain, and the transfer of the positive charge on to another PE chain such that the reaction could be repeated.

The reaction induces a number of crosslinks, not distributed in a random fashion, and eventually is terminated, e.g. by capture of an electron. The presence of electron scavengers enhances the degree of crosslinking by suppressing the termination step, hence effectively increasing the lifetime of the positive ions.

Positive ion formation in polyethylene has been reported [9], but gives different spectra to those observed in this study and is probably associated with unsaturation in the polymer. It is thought that the positive ions observed in this study are stabilized by rapid electron transfer and trapping in the system, facilitated in some way by the acrylic acid. At room temperature the ions would not be stable, but would have a sufficiently long lifetime to enable them to take part in the reaction.

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