The Sol/Gel Contribution to the Behavior of γ-Irradiated Poly(vinylidene Fluoride)

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SYNOPSIS

Poly(vinylidene fluoride) films were γ-irradiated in the dose range of 1–20 Mrad, resulting in up to 74% gel. The irradiated polymer undergoes both crosslinking and chain scission, about 5 : 3 events, respectively. Swelling measurements indicate an increasing crosslink density with the gel content, already at the lower doses. Thermal analysis of the gel fraction and the unextracted irradiated samples shows that although crosslinking affects the crystallization, degree of crystallinity, and the melting characteristics, the behavior of the crosslinked material is predominantly controlled by the extractable sol fraction which consists of the more mobile original chains, branched chains, and degraded ones. The crosslinks, already at low density, retard the development of ordinary crystalline polymer morphology.

INTRODUCTION

Ionizing radiation is known as an effective source for inducing structural changes in polymers, resulting in alterations in their physical structure and properties (e.g., Ref. 1). An irradiated polymer undergoes molecular crosslinking and/or chain scission (e.g., Ref. 2), depending mainly on the polymer chemical structure, physical state, and irradiation conditions. Although the overall effects of irradiation on the solid state structure are quite well established, the details of the structural changes taking place at the early stages of the process are generally lacking. In many industrial processes and in most published studies polymers were irradiated while in the solid state (different from melt irradiation). Solid state irradiation may thus affect the polymer structure (e.g., Refs. 3–5) and even more structural changes following subsequent recrystallization may be seen (e.g., Ref. 6). Solid state irradiation is known to produce inhomogeneous materials due to its selectivity, i.e., preferentially occurring in amorphous phase and in crystalline fold surfaces.[7,8] The resulting material properties, commonly reported, are therefore average values representing the contribution of the various polymer components. For example, in materials exposed to low irradiation doses the properties of the sol and gel fractions are averaged, and the characteristics of the extractable sol fraction has usually been ignored. A few recent studies, though limited to polyethylene, did consider both the extracted and unextracted irradiated polymer.[9]

Timmerman and Greyson[10] were the first to report the effect of ionizing irradiation (in air at room temperature) on poly(vinylidene fluoride) (PVDF). They found that radiation up to a dose of 100 Mrad resulted in reduction of the polymer density accompanied by small changes in tensile strength and elongation. These authors have suggested that their results indicate that PVDF crosslinks when irradiated. This was later confirmed[11] by studying the solubility behavior of irradiated (in vacuum of 47°C) PVDF. DSC studies coupled with X-ray analysis of electron irradiated PVDF[12] showed that the degree of crystallinity increases with an increasing radiation dose (up to 50 Mrad).

The aim of the present study is to investigate the effect of γ-irradiation, at relatively low doses, on the structure and morphology of PVDF and to shed some light on the relative contributions of the co-

existing sol and gel component fractions in the irradiated polymer. To enable comparison between the irradiated (unextracted) polymer and its gel fraction (free of extractables) all samples were melted and recrystallized by cooling under a controlled rate, prior to their thermal analyses (the structures to be discussed are therefore not characteristic of the original solid state irradiated polymer).

EXPERIMENTAL

PVDF, Kynar thin (0.25 mm) films were used as received (Pennwalt, USA). Samples were vacuum packed in sealed bags made of a flexible nylon/ polyethylene coextruded film. They were irradiated at ambient temperature, at a rate of 0.064 Mrad/h by doses ranging from 1 to 20 Mrad, using a Co^{60} source.

The gel content in the irradiated polymers was determined by extraction in dimethylacetamide (DMA) at 160°C for 48 h (until a constant weight was reached). The soluble free samples, the gel fractions, were dried in vacuum at 100°C for 24 h. Swelling ratios of the gels were also determined in DMA.

Thermal analysis was performed using a Mettler TA3000 differential scanning calorimeter (DSC) at heating and cooling rates of 10°C/min. All samples, about 10 mg, were heated from ambient temperature to 30°C above the melting temperature (first run), cooled at the controlled rate to 35°C and then reheated (second run). For calculation of degree of the crystallinity (second run), the crystalline heat of fusion (100% crystallinity content) was taken as 104.7 J/g.[13]

The surface morphology of the various annealed PVDF irradiated samples was studied using transmission electron microscopy (JEOL 100 CX). To enhance the structural details, the surface was first etched in 20% NaOH solution for 72 h. Samples were replicated (two stage cellulose acetate replicas), shadowed with Pd/Au, and carbon coated.

RESULTS AND DISCUSSION

The effect of irradiation dose on the gel content is shown in Figure 1. Interestingly, already at a dose as low as 1 Mrad the gel content is 27%. It increases rapidly to 54% at a dose of 5 Mrad, and then continues to rise moderately to 74% gel at a dose of 20 Mrad (the highest studied irradiation dose). These
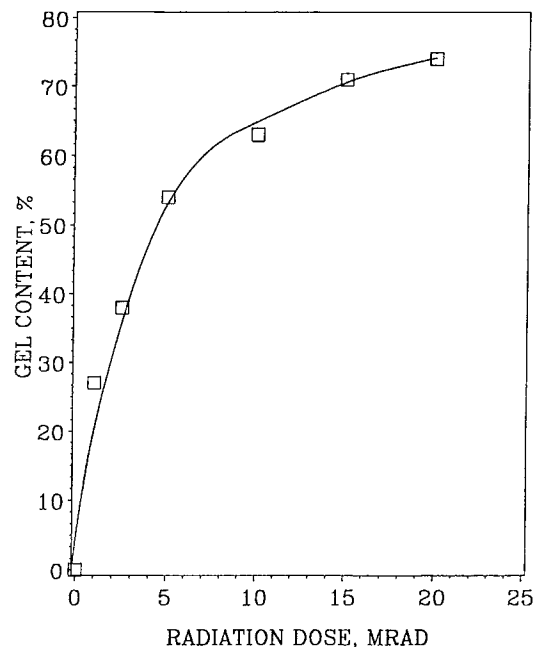
Figure 1   Gel content in γ-irradiated PVDF.

results are similar to those reported by Sands and Pezdirtz.[11] In their study a gel content of 98% was obtained at a dose of 966 Mrad. Plotting $S + \sqrt{S}$ vs. $1/R$, where S is the sol fraction in the irradiated polymer and R is the dose as in Figure 2, enables[14] to estimate the ratio of scission to crosslinking events. The extrapolation to $1/R = 0$ yields an intercept value of 0.6, namely, about three scission events occur for every five crosslinking events. Thus, the two processes take place simultaneously during exposure to ionizing irradiation of PVDF; crosslinking is the major dominating process. The increase in gel content with radiation dose is accompanied by an increasing crosslinking density, as demonstrated by the continuously decreasing swelling ratio, as in Figure 3. The shape of the curves depicting gel content and swelling as function of the radiation dose is similar, i.e., large changes during the first 5 Mrad dose and a much shallower change upon further radiation. Thus, within the 0–5 Mrad range PVDF molecules already linked to the network and additional molecules still not linked undergo net crosslinking events which increase the global crosslink density and content of gel fraction, respectively. Since the crosslink density increases simultaneously with gel content even at low irradiation doses, it is suggested that in the amorphous regions, which are known to be first affected by radiation,[7] the resulting structure is not homogeneous. The amorphous phase in itself is heterogeneous in nature, consisting of chains which exhibit different
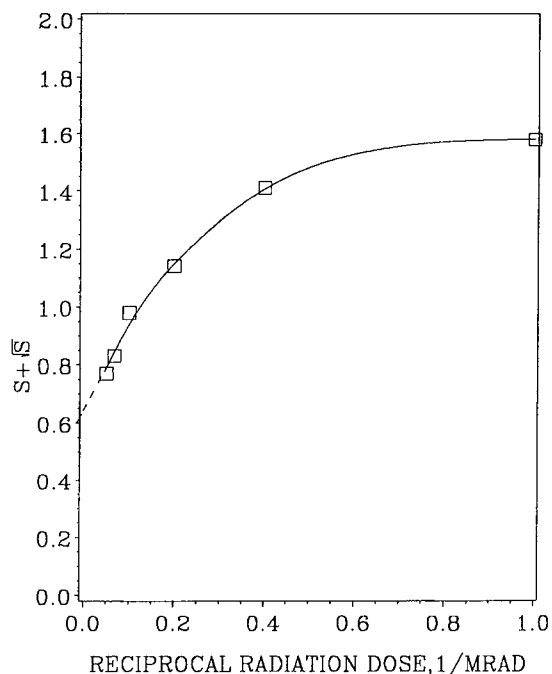
Figure 2 A plot of $S + \sqrt{S}$ vs. $1/R$ for γ-irradiated PVDF.

levels of reactivity to irradiation such as tie molecules (stretched and relaxed), chain folds, or locally, more densely packed, segments.

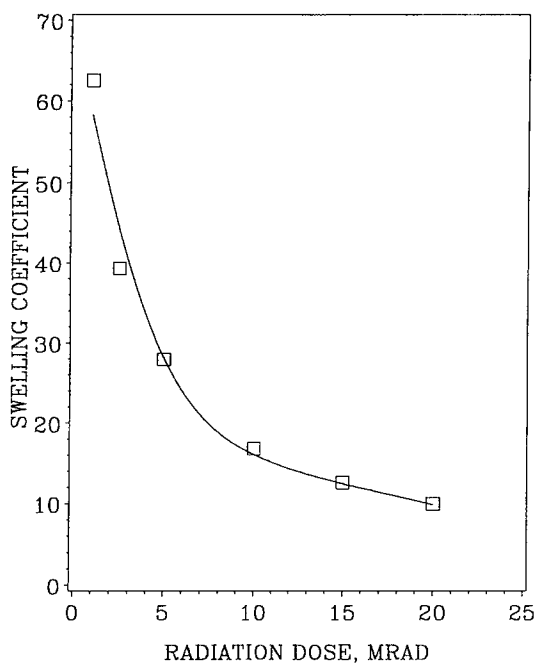The DSC thermograms of the irradiated polymer (unextracted) and those of the gel fraction, both crystallized from the melt prior to their analyses (second DSC runs), are similar in shape. All exhibit a single melting endotherm, the peak temperature of which depends on the irradiation dose. However, the dependence of the melting temperature and the degree of crystallinity (area under endotherm) on the irradiation dose for the two is rather different. As seen in Figure 4, up to 5 Mrad, the melting temperature of the unextracted polymers decreases only slightly with increasing the dose. Then it decreases more significantly, attaining its lowest value ($\Delta T_m \cong 3°C$) at 15 Mrad and upon increasing the dose to 20 Mrad the melting temperature markedly increases by 8°C. On the other hand, as shown in Figure 4, the gel fraction's melt temperature decreases linearly, and much more significantly, with the irradiation dose (ΔT_m at 20 Mrad is 7°C). It should be noted that the melting temperature of the irradiated PVDF is always higher than that of the corresponding gel. A very pronounced difference between the two series (irradiated unextracted vs. the gel fraction) is found in their degree of crystallinity, as in Figure 5. That of the irradiated PVDF first exhibits only a slight increase at low doses and then, at doses above 5 Mrad, the degree of crystallinity continuously increases; a value 7% higher than that of the original material is attained at 20 Mrad. This general trend of increasing crystallinity with dose
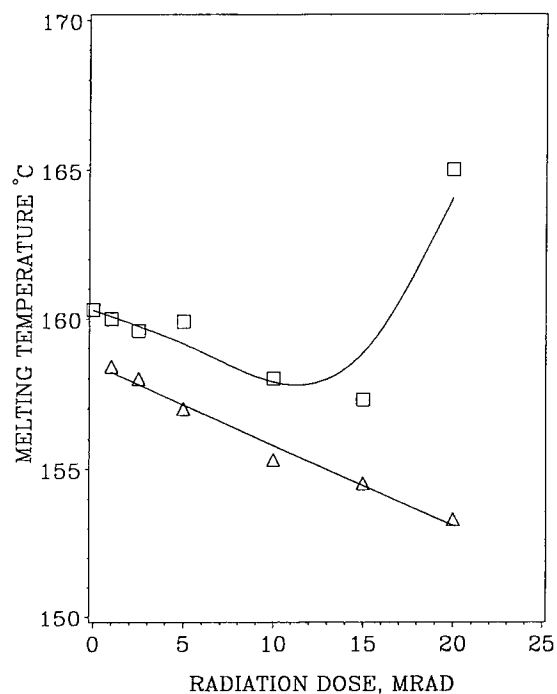

Figure 3 Swelling ratio of PVDF in DMA as affected by γ-irradiation dose.

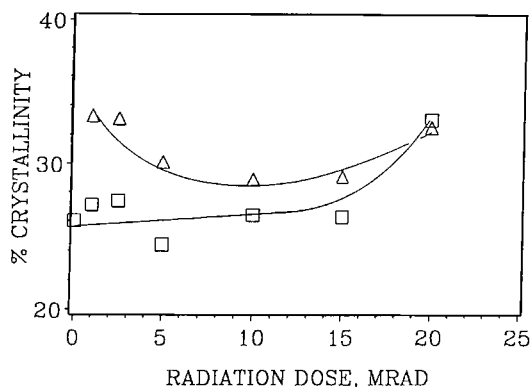**Figure 4** The melting temperature of γ-irradiated PVDF before (□) and after (△) extraction.

Figure 5 The degree of crystallinity of γ-irradiated PVDF before (□) and after (△) extraction (II run).

is similar to published literature data.[11,12] (In polyethylene such an increase in crystallinity with dose was reported only when measured from the first run thermograms.[6] The second run DSC crystallinity degree always decreased with increasing the dose.) The degree of crystallinity in the gel fraction just slightly decreases in the entire range of irradiation dose studied. It is interesting to note that the crystallinity level of the gel fraction is always higher than that of the whole irradiated samples; the difference between the two decreases with the increasing dose, becoming similar at 20 Mrad. In the present study, interestingly, the gel fractions always exhibit higher degrees of crystallinity and at the same time lower melting temperatures than the corresponding values for the unextracted irradiated PVDF. Thus, the gel fraction consists of more crystalline phase which is less thermally stable. It is therefore suggested that the soluble fraction consists of more noncrystallizable chains which are included in the original polymer as well as short chains and branched chains that are created upon irradiation. The crosslinking junctions in the gel fraction introduce more defects into the crystalline phase, resulting in smaller crystals which do not result in an additional melting endotherm in the thermograms of the unextracted polymers.

An interesting difference in the behavior of irradiated PVDF, before and after extraction, is in the polymer crystallization temperature. As depicted in Figure 6, the crystallization temperatures of both series decrease with increasing the irradiation dose; however, that of the gel exhibits significantly lower values and its rate of change with dose is markedly higher. Hence, the crystallization process of the gel fraction requires higher degrees of supercooling than that for the whole irradiated PVDF, when both are

cooled from the melt at a constant rate. This is in agreement with previous studies on the effect of crosslink density on the crystallization of polymers,[15-19] which all concluded that crosslinking reduces the rate of crystallization in crosslinked melts. Moreover, considerable differences were reported[9] in the crystallization of extracted and unextracted chemically crosslinked polyethylene. In the present study, the presence of up to 74% gel fraction results in only a slight decrease in the peak crystallization temperature; thus, the remaining sol fraction seems again to dominate the crystallization process. However, the significant crystallization temperature reduction in the extracted gels and its dependence on crosslinking density indicate that the crosslinks have a large influence in restricting chain mobility, especially that of diffusional mobility essential for crystallization. Still surprising, as mentioned above, is the low effect produced by the presence of appreciable gel content on the crystallization temperature of the unextracted irradiated PVDF, which is different from irradiated polyethylene behavior.

The surface morphology of irradiated annealed PVDF films and their corresponding gel fractions was also studied. To enhance the structural details, required for low crystallinity content polymers, samples were etched (NaOH solution) prior to their replication. Therefore, the observed surface struc-
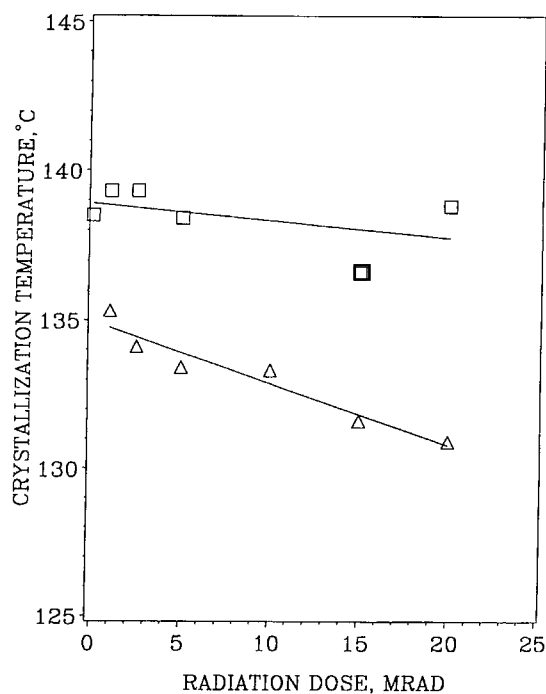

Figure 6 The crystallization temperature of γ-irradiated PVDF before (□) and after (△) extraction.
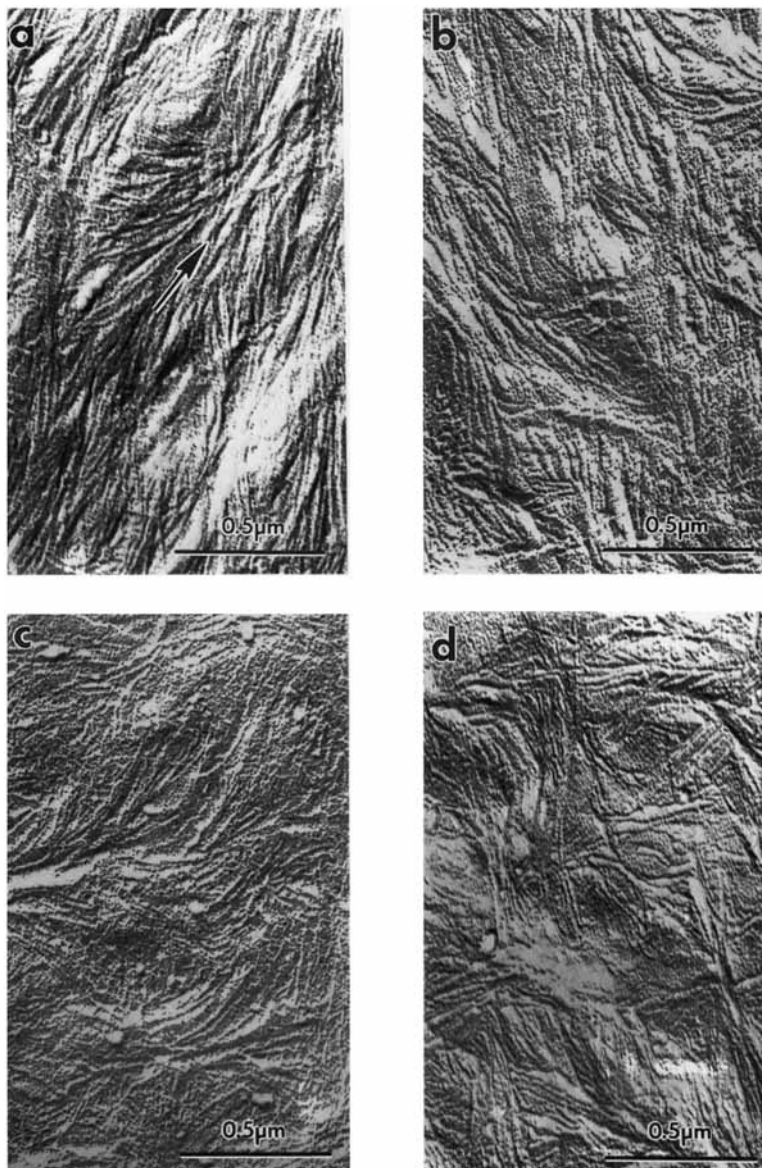
Figure 7   Electron micrographs of γ-irradiated and 100°C annealed PVDF [Mrad (Pd/
Au–C replica)]: (a) 1; (b) 5; (c) 10; (d) 20.

ture represents the different reactivities of the various morphological entities with respect to the etchants (using this technique some artifacts can be introduced). Unirradiated PVDF films and annealed irradiated samples exhibit the common spherulitic or lamellar surface structures (Fig. 7). It seems that surfaces of films exposed to the higher doses exhibit deeper gaps between lamellae seen edge on, and shorter and less developed lamellar structures. It should be emphasized that these observed morphological changes are not suggested to occur during the radiation process (at ambient temperature), but during the annealing because of the increasing mo-

bility of sol fraction chains which exist in the polymer. These observations are due to changes, as a result of γ-irradiation, in the resistance of the various regions of the polymer to NaOH etching, with the increasing gel content and crosslinking density.

The surface morphology of the gel fraction is very different from that of the solid state irradiated unextracted PVDF. It should be noticed that the irradiated PVDF has been crystallized prior to its irradiation and annealed afterwards, whereas the gel crystallized upon cooling the swollen crosslinked polymer and annealing in the oven. The gel's surface is nodular in nature (Fig. 8), though in some regions
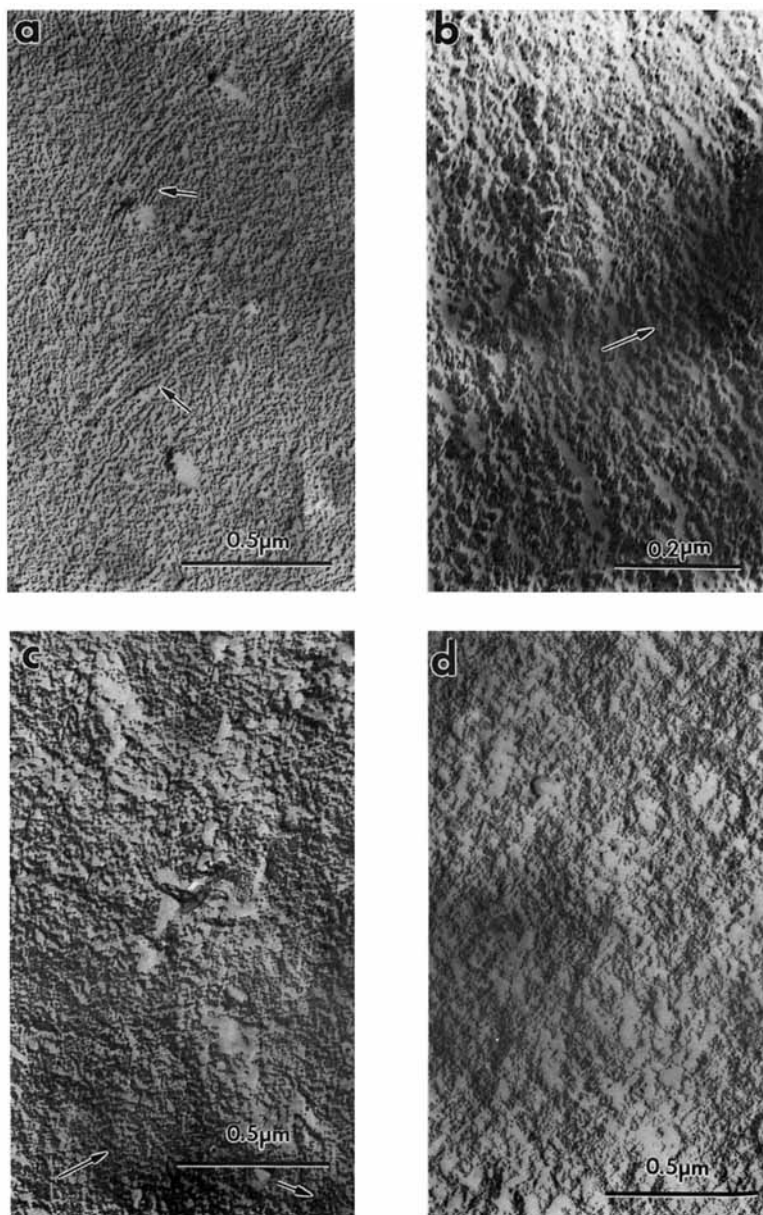
Figure 8 Electron micrographs of γ-irradiated PVDF dry gel Mrad [(Pd/Au–C replica)]: (a) 1; (b) 5; (c) 10; (d) 20.

[Fig. 8(a)] sheaves of parallel short lamellae can be observed. The oriented lamellar growth suggests crystallization under stress. These short lamellae are much thinner than those observed in the as irradiated samples, probably due to the restricting crosslinking junctions. This difference in lamellar thickness could be contributing to the lower melting temperatures of the gel fractions, as discussed above. In gel fractions obtained from samples irradiated at the higher studied doses, it is becoming quite difficult to identify any lamellar structure among the nodules, which cover the entire surface. In Figures 8(b) and 8(c), some nodules are arranged in parallel line, indicating the existence of lamellar structure while the surface shown in Figure 8(d) seems "amorphous" (all samples are crystalline according to thermal analysis). The difficulties encountered in studying the surface morphology indicate an increasing chemical resistance to the etchant by the crosslinked polymer. Crosslinking of polyethylene also retards the development of conventional spherulitic structure[20,21]; instead, sheaf or bundlelike morphologies were observed. However, lamellar organization prevailed at all levels of crosslinking.

The thermal analysis and the microscopic study of low dose γ-irradiated PVDF and their corresponding gel fractions suggest that the crystallization and the crystal properties and arrangement in the gel and in the irradiated PVDF are different. The thermal analysis suggests a dominant role played by the sol fraction in the irradiated PVDF. The presence of extractables, the more mobile species in the system, even at the relatively lower percentage, exerts a significant effect on the crystallization and melting behavior of the crosslinked polymer. The level of extractables is decreasing with the irradiation dose; however, due to branching and chain scission events its composition is continuously changing. γ-Irradiated PVDF, similar to other crosslinked polymers, may be considered as an intimate blend system. The compatibility of its components, gel and sol, especially in the crystalline phase, should be a subject for further investigation.

REFERENCES

1. A. K. Mukherjee, B. D. Gupta, and P. Sk. Sharma, *JMS-Rev. Macromol. Chem. Phys.*, **C26**, 415 (1986).
2. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Wiley, New York, 1962.
3. D. R. Gee and T. P. Melia, *Polymer*, **11**, 178 (1970).
4. W. K. Busfield and J. H. O'Donnell, *Eur. Polym. J.*, **15**, 379 (1979).
5. M. Narkis, A. Tzur, A. Vaxman, and H. G. Fritz, *Polym. Eng. Sci.*, **25**, 857 (1985).
6. M. Narkis, I. Raiter, S. Shkolnik, A. Siegmann, and P. Eyerer, *J. Macromol. Sci. Phys.*, **B26**(1), 37 (1987).
7. G. N. Pattel and A. Keller, *J. Polym. Sci. Polym. Phys. Ed.*, **13**, 303 (1975).
8. G. N. Pattel and A. Keller, *J. Polym. Sci. Polym. Phys. Ed.*, **13**, 323 (1975).
9. Y. H. Kao and P. J. Phillips, *Polymer*, **27**, 1669 (1986).
10. R. Timmerman and W. Greyson, *J. Appl. Polym. Sci.*, **6**(22), 456 (1962).
11. G. D. Sands and G. F. Pezdirtz, *Polym. Prepr.*, **6**, 987 (1965).
12. K. D. Pae, S. K. Bhateja, and J. R. Gilbert, *J. Polym. Sci. Polym. Phys. Ed.*, **25**, 717 (1987).
13. D. W. Vankerselen and P. J. Hoftyzer, *Properties of Polymers*, Elsevier, Amsterdam, 1976.
14. A. Charlesby and S. H. Pinner, *Proc. Roy. Soc. London*, **249**, 367 (1959).
15. A. N. Gent, *Trans. Faraday Soc.*, **50**, 521 (1954).
16. A. N. Gent, *J. Polym. Sci. A*, **3**, 3787 (1965).
17. A. N. Gent, *J. Polym. Sci. A-2*, **4**, 447 (1966).
18. E. H. Andrews, P. J. Owen, and J. Singh, *J. Proc. Roy. Soc.*, **A324**, 79 (1971).
19. P. J. Phillips and Y. H. Kao, *Polymer*, **27**, 1679 (1986).
20. R. M. Gohil and P. J. Phillips, *Polymer*, **27**, 1687 (1986).
21. R. M. Gohil and P. J. Phillips, *Polymer*, **27**, 1696 (1986).