

Radiation-Induced Crosslinking of Acetylene-Impregnated Polyesters. II. Effects of Preirradiation Crystallinity, Molecular Structure, and Postirradiation Crosslinking on Mechanical Properties

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ABSTRACT: Electron beam-irradiated crosslinking has been studied in a series of acetylene-impregnated polyesters and amorphous copolyesters, including poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), poly(cyclohexane dimethylene terephthalate) (PCDT), and poly(cyclohexane dimethylene terephthalate-co-ethylene terephthalate) (P(CDT-co-ET)) having 29 and 60 wt % ethylene terephthalate (ET). The extent of crosslinking was observed by gel fraction measurements and was found to be significantly influenced by the aliphatic chain content of the polyesters (PET < PBT < PCDT). In addition, as the preirradiation crystallinity of the polyesters was reduced, the extent of acetylene-enhanced crosslinking was greatly raised. Decreases in the postirradiation crystalline melting temperature and degree of crystallinity were observed in all the polyesters, using differential scanning calorimetry measurements. Particularly significant findings have been the

shift in the glass-transition temperatures (T_g) to higher temperatures and the decrease in loss tangents at higher temperatures, both of which confirm that crosslinking has taken place. The storage moduli (E') in the rubbery plateau region of PCDT and P(CDT-co-ET) were significantly affected by irradiation dose. Increased network tightness in postirradiated PBT and PCDT films was also inferred from melt-rheology measurements, in which stress relaxed more slowly following a stepped strain. Improvements in the mechanical properties of the irradiated polyesters and copolyesters were clearly evidenced by the increased modulus at higher temperatures, observed using dynamic mechanical thermal analysis and melt-rheology methods. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4476–4490, 2006

Key words: crosslinking; irradiation; polyesters; mechanical properties; rheology

INTRODUCTION

Previous radiation studies of poly(ethylene terephthalate) (PET)^{1,2} have shown that high doses are required for reasonable levels of crosslinking to be achieved. This is because the alkyl radical, which is the predominantly observed reactive species,³ is prone to undergo rapid β -bond scission, resulting in the production of the carboxyl radical.^{3,4} Hydrogen atom transfer reactions then ensure continued formation of fresh alkyl radicals; hence, main chain scission is seen to occur as part of cyclic chain reaction mechanisms.^{3–5} Bell and Pezdirtz² demonstrated that higher levels of crosslinking can be obtained by increasing the alkyl chain length of the glycol segment, from PET through poly(butylene terephthalate) (PBT) to poly(decamethylene terephthalate) (PDMT), following in vacuo irradiation. The increasingly higher levels of crosslinking resulted

from the diminishing probability that alkyl radicals will be formed subjacent to the weak side of the ester linkage. Hence, cyclic β -bond main chain scission becomes ever less probable.⁵ However, even when increasing the alkyl chain length, Bell and Pezdirtz found that high doses were required before insoluble (gel) fractions were achieved (PBT $\sim 1000 \times 10^4$ Gy, PDMT $\sim 200 \times 10^4$ Gy). In addition, this technique also suffers from the limitation that, as the alkyl chain length is increased, the polyester becomes more polyalkane-like and unsuitable for the task it was originally intended.

Similarly, in a recent study on the radiation-induced crosslinking of acetylene-impregnated polyesters,⁵ the present authors observed reduced main chain scission and increased extents of crosslinking to arise from increasing the alkyl chain length of the glycol segment (PET through PBT to poly(cyclohexane dimethylene terephthalate) (PCDT)). More importantly, the use of acetylene was demonstrated to greatly reduce the extent of cyclic main chain scission and increase the extent of crosslinking in the amorphous regions. High

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degrees of crosslinked networking were achieved by combining the two techniques (increased alkyl chain length and acetylene impregnation), such that high gel fractions were obtained in thin films and fibers of PCDT and PBT, at relatively low doses. However, although gel fractions were increased in PET by impregnating acetylene, only a small improvement factor of about 2.5 was achieved and high doses were still required. It was also noticeable in the same study that PBT gel fractions, obtained using the constant volume (CV) annealing regime with acetylene, decreased with increasing sample thickness. Since ample time was given for complete equilibrium diffusion of acetylene in the thin fibers and films, and since acetylene does not penetrate the crystalline regions of these polymers, it was assumed that these effects were at least in some part due to variations in the degree of crystallinity. Higher degrees of crystallinity are expected to yield lower extents of crosslinked network formation. If this is true, then the effect of the degree of crystallinity on the crosslinking of the polyester samples is important, having wide implications. Thus, further morphological studies of acetylene-impregnated, irradiated, and annealed polyesters became necessary. The current study was carried out to probe the effects of morphology on the polyesters of the previous study (PET, PBT, and PCDT).⁵ In addition, two random copolyesters of poly(1,4-cyclohexane dimethylene terephthalate-co-ethylene terephthalate) (P(CDT-co-ET)) having 29 and 60 wt % ET have been examined. Copolyesters of this type have a reduced tendency to crystallize and yield important information as to effect of crystallinity. Post-irradiation analytical techniques, including gel fraction by solvent extraction, differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and melt rheology, were applied to acquire structural information on the irradiated polyesters.

EXPERIMENTAL

Materials

PET films (0.015 and 0.225 mm), PET fibers (273,150/33, $M_{n,o} = (1.97 \pm 0.20) \times 10^4$ mol/g, diameter = 2.174×10^{-2} mm), PBT chips ($M_{n,o} = (2.23 \pm 0.22) \times 10^4$ mol/g), and PBT fibers (273,150/33, $M_{n,o} = (2.53 \pm 0.25) \times 10^4$ mol/g, diameter = 2.216×10^{-2} mm) were supplied by the Hoechst-Celanese Corp., USA. PCDT films (0.0085 mm) were supplied by Diafoil-Hoechst Co. Ltd., Tokyo. Amorphous copolyesters of P(CDT-co-ET) chips (29 and 60 wt % ethylene terephthalate (ET)) were obtained from Aldrich Chemical Co. Ltd. Atomic absorption-grade acetylene gas was supplied by British Oxygen Co. Ltd. 2-Chlorophenol and 1,2-dichlorobenzene were obtained from Aldrich Chemical Co. Ltd.

Sample preparations

Polyester films and fibers were used as received without further purification, other than drying overnight in a vacuum oven at 70°C. PBT and P(CDT-co-ET) chips were pressed into sheets between brass plates covered with Teflon film (Tygaflor) at 263°C and 290°C, respectively. The polyester chips were melted in a press for 5 min prior to pressing at 2.8 MPa for 2 min, followed by immediate quench cooling in cold water.

Impregnations

The samples were cut to size, placed in sealed tubes, and evacuated of air gases for at least 1 h. The polyesters were impregnated with acetylene gas by filling the tubes to atmospheric pressure with acetylene ($\sim 1.013 \times 10^4$ Pa) and allowing the gas to penetrate into the samples by normal diffusion processes for 24 h. The diffusion times were calculated to be more than sufficient to remove atmospheric oxygen and impregnate acetylene into PET films, for which diffusion data already exists. In addition, 2 h before irradiation, the excess gas in the tubes was quickly evacuated and replaced with fresh acetylene.

Irradiations

All samples were irradiated with electron beam, using a Van de Graaff Electron Accelerator (High Voltage Engineering Corp., Model K; 3 MeV) at the University of Leeds Cookridge Radiation Research Centre (CRRC). Absorbed doses were determined using red perspex absorption dosimeters (AERE Harwell, Oxon, type 4034R; $\lambda = 640$ nm). Doses are expressed in units of Gray (Gy; 10^4 Gy \approx 1 Mrad). The irradiations of all the polyesters were carried out at room temperature.

Annealing

Following irradiation, all samples were annealed at a specific temperature below the melt for 1.5 h, while in an acetylene atmosphere. The irradiations, and more particularly annealings, were conducted under constant pressure (CP). Excess pressure caused by irradiation heating or annealing was automatically vented.

Gel fractions

Irradiated polyester samples (0.125–0.175 g) were placed in weighed stainless steel gauze containers (120 mesh), refluxed for 48 h, dried under vacuum (12 h at 80°C), and reweighed. Gel fractions were calculated as the dried sample weight after refluxing divided by the initial sample weight.

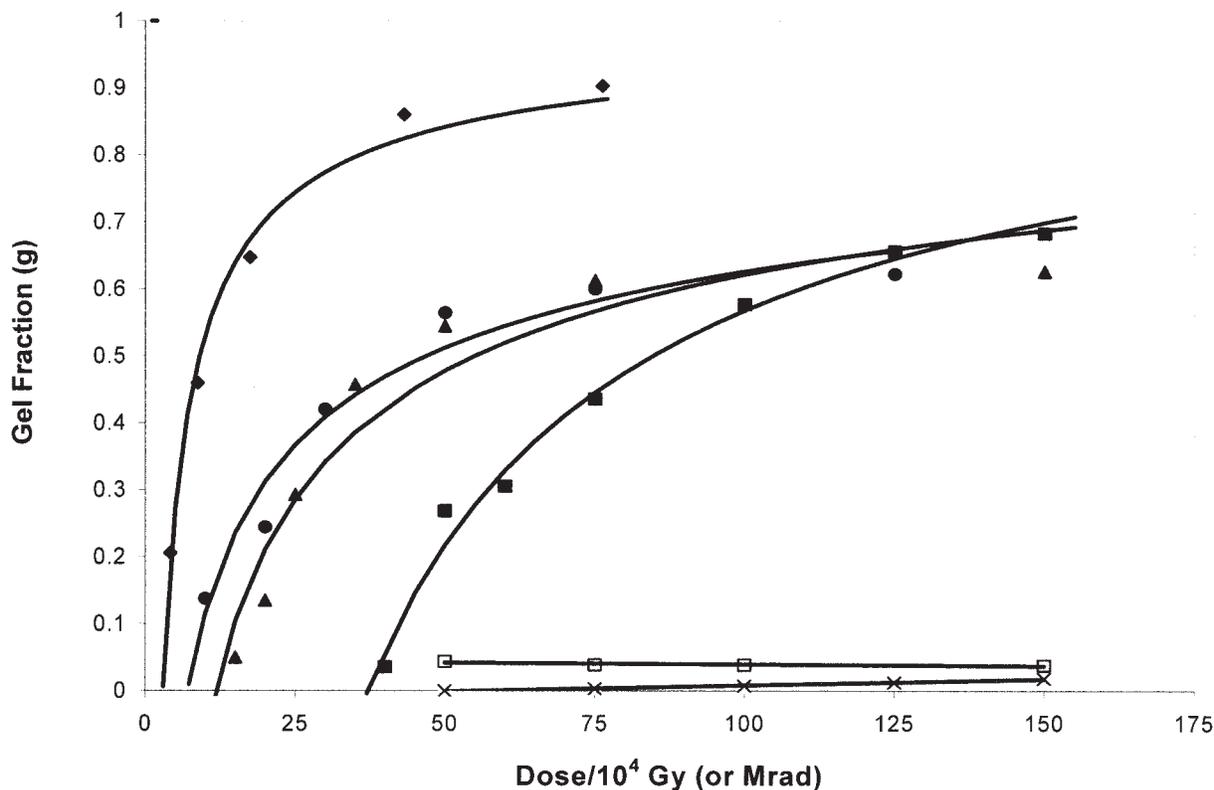


Figure 1 Gel fraction results of irradiated polyesters and copolyesters (×, PET film; 127, PET fiber; ■, PBT film; ◆, PCDT film; ●, P(CDT-co-ET) 29 wt % ET film; and ▲, P(CDT-co-ET) 60 wt % ET film).

Differential scanning calorimetry

DSC measurements were performed on a Perkin–Elmer DSC7 system with a control cooling accessory. The instrument was calibrated prior to use with indium (156.6°C, 28.5 J/g) and zinc (419.5°C). The DSC scans were performed twice on each sample of 5–10 mg, encapsulated in aluminum pans. Results were obtained using a scanning rate of 10°C/min, second run.

Dynamic mechanical thermal analysis

Viscoelastic properties of the electron beam-irradiated polyesters were investigated, below the respective melting temperatures, using a Rheometrics Solids Analyzer (RSA II), with fibers or film fixtures in tension mode. Measurements of storage (E'), and loss (E'') moduli and damping ($\tan \delta$) were made at 5°C and 20°C increments, using a dynamic sinusoidal strain of 0.05% applied at a frequency of 1.5 Hz. Samples were equilibrated at each temperature for 1 or 3 min before measurements were made. Liquid nitrogen was used as the furnace coolant, allowing temperature scans from –150 to 250°C.

Melt rheology

Measurements on irradiated PBT and PCDT films were made using a Rheometrics Dynamic Analyzer

(RDA II). Discs of polyester films were dried under nitrogen in a vacuum oven at 100°C overnight and vented to nitrogen before transfer to the RDA II. Dynamic viscoelasticity measurements were carried out with the cylindrical samples between parallel disc platens (7.8 mm diameter). Shear deformation was applied about the cylinder axis, either in oscillation to determine the in-phase (storage) and quadrature (loss) dynamic moduli, G' and G'' , respectively, or as a stepped strain to obtain the relaxation modulus, $G(t)$. All measurements were determined in a nitrogen atmosphere and carried out isothermally at 230°C and 290°C for PBT and PCDT, respectively. The strain level was determined from a strain sweep, which gives maximum torque within the linear limit.

RESULTS AND DISCUSSION

Gel fractions

Gel fraction data collected from the polyesters irradiated and annealed under CP are shown in Figure 1. As for our previous study,⁵ it was not possible to obtain high gel fractions from PET films and fibers. The lowest dose at which the gel fraction could be obtained (D_g) was about 48×10^4 and 25×10^4 Gy for PET films and fibers, respectively. Normally, in the absence of acetylene, the gel point is not found until even higher

TABLE I
Estimated Values of the Degree of Diffusion (Z) for Acetylene in PET, PBT, and PCDT Films and Fibers with Different Size and Degree of Crystallinity

Polyesters	Conditions		Z for O ₂ out (1 h)	Z for C ₂ H ₂ in (24 h)
	Diameter or thickness (mm)	Degree of crystallinity (%)		
PET films	0.015	28.0	1.0000	1.0000
	0.225	35.8	0.5212	0.7720
PET fiber	0.022	35.3	1.0000	1.0000
PBT films	0.100	34.4	0.9436	0.9987
	0.300	41.4	0.3972	0.6028
PBT fiber	0.022	29.3	1.0000	1.0000
PCDT films	0.009	35.9	1.0000	1.0000
	0.060	33.2	1.0000	1.0000
	0.080	33.5	1.0000	1.0000
	0.200	32.1	0.8745	0.9909
P(CDT-co-ET)				
29 wt % ET	0.200	Amorphous	0.8223	0.9791
60 wt % ET	0.200	Amorphous	0.7423	0.9487

doses are used (120×10^4 Gy following in vacuo irradiation).¹ Hence, it can be concluded that acetylene had increased the extent of crosslinking and inhibited scission processes considerably.

Improved gel fractions were obtained by increasing the alkyl chain length of the ester linkage from PET (two carbon atoms) to PBT (four carbon atoms). Greatly enhanced gel fractions were obtained from samples of PBT fibers, but there was no evidence of increased gel formation from in-house prepared PBT films (0.3 and 0.1 mm thickness), even though the two polymers had similar Mn,o. Estimations of the relative degree of diffusion (Z) for oxygen "out" of and acetylene "into" the polyesters films and fibers with different size and degree of crystallinity from DSC measurements are given in Table I.⁶⁻⁸ The impregnation time was sufficient to allow a high degree of diffusion of acetylene into all but the very thickest PBT sample (0.3 mm), and even this sample had a calculated Z value of 0.603 (or 60.3%). The evacuation time was also sufficient to allow a high degree of oxygen evacuation out of all but the very thickest PBT (0.3 mm) and PET (0.225 mm) samples, which had calculated Z values of 0.397 (39.7%) and 0.521 (52.1%), respectively. Hence, some enhanced crosslinking should have been observed even in the 0.3 mm PBT in-house prepared film. The 0.1 mm PBT film certainly had sufficient evacuation ($Z_{O_2} = 0.944$) and impregnation ($Z_{C_2H_2} = 0.999$) for fully enhanced crosslinking. The only other major difference between the PBT fibers (2.216×10^{-2} mm diameter, Z_{O_2} and $Z_{C_2H_2} = 1$) and the in-house prepared 0.1 mm PBT film was the degree of preirradiation crystallinity, being 29.3% and 34.4%, respectively. The crystallinity of the in-house prepared 0.3 mm PBT film was also very high (41.4%). Hence, it can be assumed that the main reason for the lack of enhanced crosslinking in the in-house prepared PBT

films was the high degree of crystallinity of the samples. The same effect was observed from the thicker PET films prepared in-house. PBT and other linear aromatic polyesters, such as PET, are known to crystallize rapidly, because of the high temperatures and ease with which crystallization takes place. Acetylene is unable to penetrate the crystallites and leaves them completely unprotected from β -bond scission. In addition, high degrees of crystallinity leave fewer paths for gas transport between the crystallites. The Dg of the PBT fiber ($\sim 25 \times 10^4$ Gy) was not improved from that of PET under equivalent conditions; however, the PBT fibers yielded increasingly higher gel fractions for equivalent doses thereafter, until a gel fraction of 70% was obtained at 150×10^4 Gy. In the previous study,⁵ under CV conditions, where excess pressure above atmospheric was not vented, enhanced gel fractions were achieved in both PBT films (0.25 mm thickness) and fibers (2.216×10^{-2} mm diameter). Both these sets of data indicate that, providing the crystallinity is kept low, increasing the glycol chain length by two methylene units reduces the probability of β -bond scission and increases the extent of crosslinking significantly, but not to a useful degree. The data also demonstrate that higher pressures of acetylene overcome the increased energy barriers to gas transport between the amorphous regions that result in samples of higher crystallinity.

In the current study, gel fractions were more greatly enhanced by increasing the alkyl chain length further to PCDT (eight carbon atoms). The higher degrees of crosslinking achieved in the acetylene-impregnated PCDT films are comparable to those achieved in PE. For example, with dose of 50×10^4 Gy in the presence of acetylene, the gel fraction found for the PCDT was 0.84, whereas Jones et al.^{8,9} obtained ~ 0.80 for HDPE fibers and ~ 0.95 for LLDPE film. The increased gel

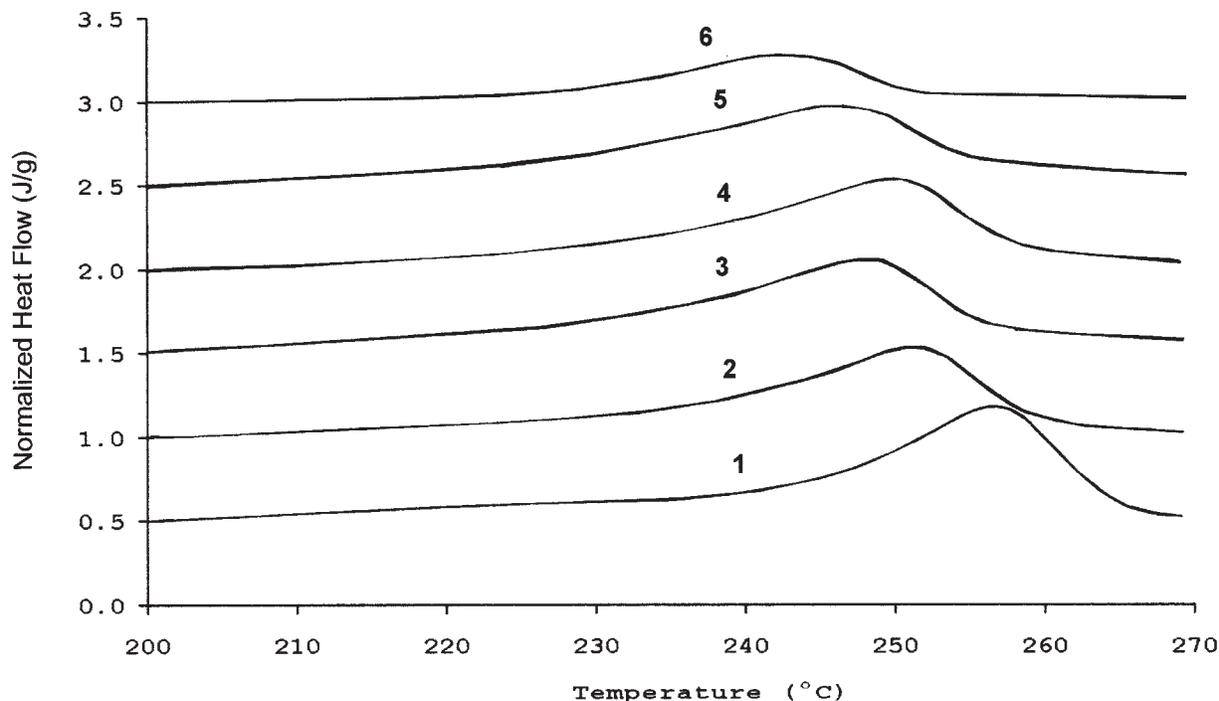


Figure 2 Comparison of the DSC thermograms for PET fibers before and after irradiation with increasing doses; 0, 50, 75, 100, 125, and 150×10^4 Gy (or Mrad) for 1, 2, 3, 4, 5, and 6, respectively.

fraction for PBT and PCDT resulted from the increased extent of crosslinking and decreased proportion of β -bond scission in these polyesters, which in turn can be attributed to increasing the aliphatic chain length in the presence of acetylene. Such increases in the degree of crosslinking and decreases in main chain scission were observed in our previous work,⁵ and to a lesser extent, in that of Bell and Pezdirtz.² The latter study demonstrated an increase in viscosity when increasing the aliphatic chain length from PET though PBT to PDMT, following the degree of in vacuo irradiation. In the current study and our previous study, we found dramatic increases in gel fraction when acetylene is also used in conjunction with increasing the aliphatic chain length in situations of low crystallinity.

Turning to the copolyesters of PCDT and PET, P(CDT-co-ET), it can be seen, not unexpectedly, that the gel fractions are slightly less enhanced than for PCDT alone, but are much greater than for PBT alone. At first sight, it could be assumed that the gel fraction curves of the P(CDT-co-ET)s can be ascribed to the proportional effects of the two aliphatic chain lengths of PCDT and PET. However, with the exception of the lowest dose data set, which are most prone to error, the 29% ET and 60% ET P(CDT-co-ET) polymer data yield almost identical gel fraction curves. Hence, the proportion of ET in the copolyesters appears to be of little consequence. From previous studies on alkyl polymers² and aromatic polyesters⁵ and knowledge of

molecular dimensions, it is known that acetylene enhances crosslinking only in the amorphous regions, because it does not penetrate into the crystallites. This was demonstrated by the PBT film and fiber in the present study. Hence, it appears that so long the crystallinity of the polyester is reduced sufficiently, and therefore, β -bond scission is inhibited by acetylene ingress, and enhanced crosslinking will be greatly achieved. It can be seen here that this can be easily accomplished by the use of additional polyesters, as copolyesters.

Differential scanning calorimetry

The crystalline melting temperatures and degree of crystallinity in the polyesters were both observed to decrease following irradiation, by DSC measurements. This was particularly noticeable in highly crystalline PET and PBT fibers, as shown in Figures 2 and 3. It was found that the melting temperature of PET and PBT fibers decreased by $\sim 22^\circ\text{C}$ and 15°C , respectively, following irradiation (150×10^4 Gy) in the presence of acetylene. Kusy and Turner¹⁰ observed a decrease of approximately 25°C in the melting temperature of PET, following completely unprotected (in vacuo) irradiation at 2000×10^4 Gy. These results generally indicate that dose-dependent crystalline destruction had occurred. In the current study, crystalline destruction occurred because acetylene did not penetrate the crystallites and inhibit β -bond scission within them.

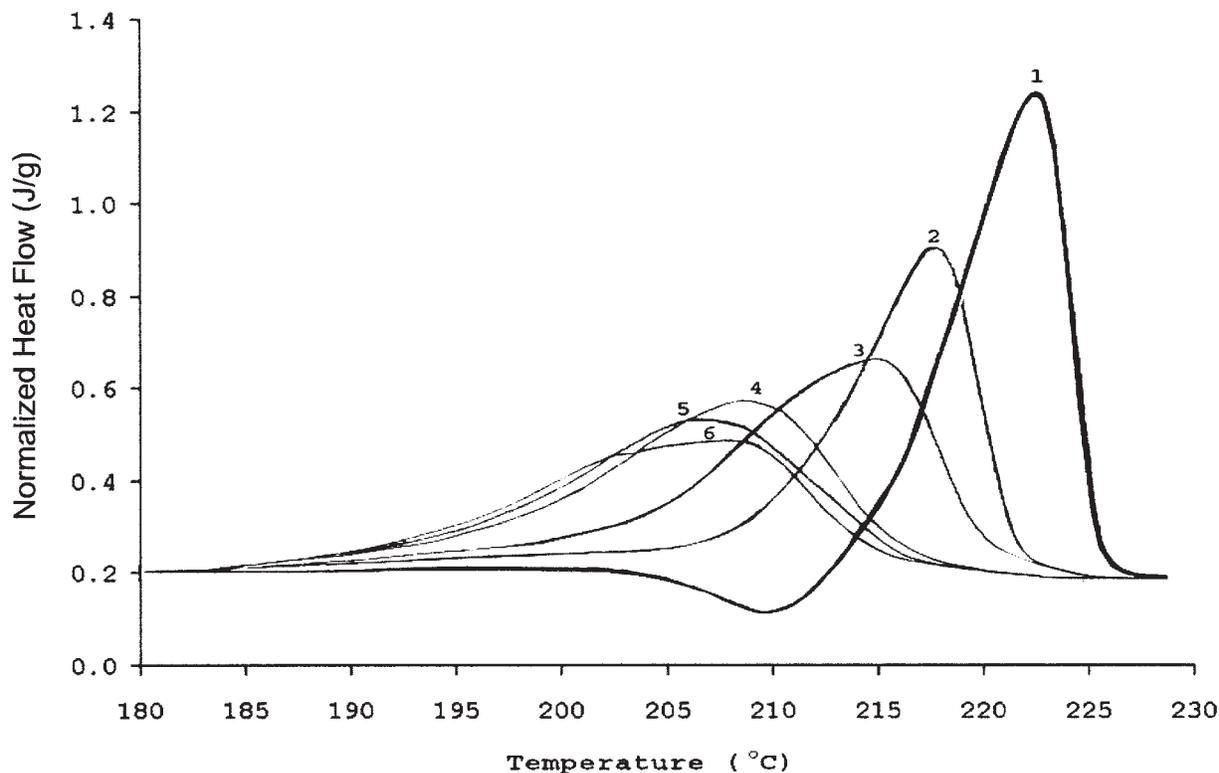


Figure 3 Comparison of the DSC thermograms for PBT fibers before and after irradiation with increasing doses; 0, 50, 75, 100, 125, and 150×10^4 Gy (or Mrad) for 1, 2, 3, 4, 5, and 6, respectively.

The effect of unprotected irradiation on the crystalline regions is to cause imperfections. Previous studies of the structure and morphology of irradiated PE¹¹⁻¹³ led to proposals for the observed melting behavior of the polymer. Significant information was obtained concerning the location of crosslinks and chain scissions. These authors postulated that crosslinks are formed in the amorphous phase and at lamellar fold surfaces of PE, while chain scission reactions occur at all unprotected sites within the morphology. In addition, it has been suggested that alkyl radicals are able to migrate from the inside of PE crystallites to the lamellar fold surfaces.^{9,11,13,14} The experimental evidence in the current study also suggests that enhanced crosslinking takes place in the amorphous regions and at the amorphous-crystalline interface. Hence, the change in melting temperature and degree of crystallinity of PET and PBT fibers results mainly from crystallite destruction. This may be taken as further evidence that the crystallites are not protected by acetylene and are gradually destroyed by β -bond scission. It may be that, additionally, crosslinks at the surface of crystallites also reduce the melting temperature to some extent, but this effect cannot possibly be as great as the damage caused by β -bond scission, crystallite destruction.

It has been seen from the gel fractions that the P(CDT-co-ET) copolyesters readily undergo radiation-

induced, crosslinked, network formation in the presence of acetylene, because they possess little or no preirradiation crystallinity. The absence of preirradiation crystallinity was observed in that the nonirradiated P(CDT-co-ET) films (0.2 mm, 29 and 60 wt % ET) exhibited no obvious melting endotherm. Thus, these copolyesters were completely amorphous and unsuitable for postirradiation DSC studies, because the technique predominantly monitors crystalline changes.

Dynamic mechanical thermal analysis

The effect of irradiation and annealing, in the presence of acetylene, on the dynamic mechanical properties of PET, PBT, PCDT, and P(CDT-co-ET) films are shown in Figures 4-9. For PET and PBT films (Figs. 4 and 5), it is clear that the change in storage modulus (E') with temperature, above the glass transition temperature (T_g) in the rubbery region, was larger for the irradiated films than for the nonirradiated films. For all doses, the E' modulus above the T_g increased slightly. We believe that the increase in E' modulus, at these temperatures, results from the stiffness of the radiation-induced crosslinked networks. Crosslinking of the PET and PBT films had very little effect on the magnitude of the respective E' values at low temperatures. Crosslinking does, however, raise the T_g by introducing restrictions on the molecular motions of

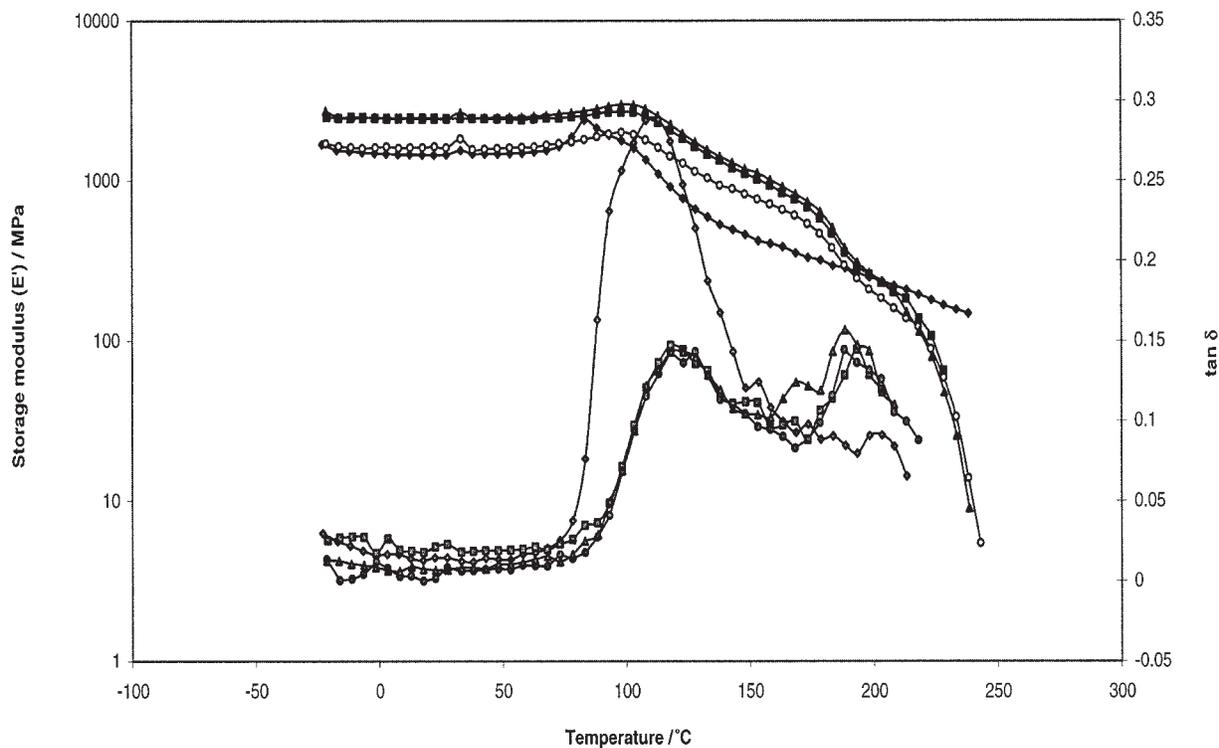


Figure 4 Comparisons of storage modulus (E') and $\tan \delta$ at 0.05% strain and 1.5 Hz for PET film before and after irradiation with different doses (\blacklozenge , E' (0 Mrad); \blacksquare , E' (50 Mrad); \circ , E' (100 Mrad); \blacktriangle , E' (150 Mrad); \blacklozenge , $\tan \delta$ (0 Mrad); \blacksquare , $\tan \delta$ (50 Mrad); \circ , $\tan \delta$ (100 Mrad); and \blacktriangle , $\tan \delta$ (150 Mrad)).

the chain.⁸ It can be seen clearly that irradiation and annealing of the acetylene-impregnated PET and PBT films raises the T_g by 15–20°C relative to that of the nonirradiated material. The broadening of the damping peaks ($\tan \delta$) in the irradiated films is attributed to the broadened distribution of molecular weights between crosslinks and heterogeneity in the network structure.¹¹ Both of these features are generally observed in crosslinked PET and PBT films. However, crosslinking did not influence the moduli values as noticeably as it influenced the T_g values. Crosslinking should increase the elastic modulus at high temperatures. There is also some evidence for PET and PBT in Figures 4 and 5 that the E' modulus begins to reverse a little at higher doses, probably because of the effect of chain scissions within the crystalline regions. The chain scission almost certainly resulted from unprotected, crystallite-trapped radicals, which are known to occur in irradiated crystalline polyesters. Conclusions from the DMTA results for PET and PBT films can best be made on the basis of the $\tan \delta$ peaks. The changes that were found in the dynamic elastic modulus and the internal friction following irradiation were attributed primarily to a combination of the following effects: the destruction of crystallinity, the introduction of crosslinks, and main chain scission processes.

Enhanced levels of crosslinking were also observed by DMTA of PCDT and P(CDT-co-ET) films (Figs.

6–9). Firstly, crosslinking raised the T_g and produced an increase in the E' modulus in the rubbery and melt regions of PCDT and the copolyesters. The drop in E' , observed in nonirradiated samples, was shifted to higher temperatures. This can be seen clearly in PCDT films of different thicknesses. Secondly, the T_g transition region was broadened, with the modulus dropping at a lower rate, giving rise to a plateau at a much higher level, because the nature of the polymer backbone had changed as result of crosslinking, and to a lesser extent, by main chain scission in the crystallites in PCDT. It is unlikely that scission processes played a significant role in the P(CDT-co-ET) films, because these polymers were almost completely amorphous. Finally, the $\tan \delta$ peak height decreased because of the combined effects of reduced segmental motion and perturbed relaxation of the chains resulting from structural modification.

The effect of crosslinking appears to be much greater in PCDT than was observed for PET and PBT, but less for the copolyesters. This is probably because the modulus in the rubbery region of PBT and PCDT has a large component because of crystalline-entrapped chains, which does not exist in the copolyesters, given that they are completely amorphous. The changes in modulus indicate that decreasing the crystallinity and increasing the proportion of PCDT in the amorphous copolyesters improves the mechanical properties at high temperatures.

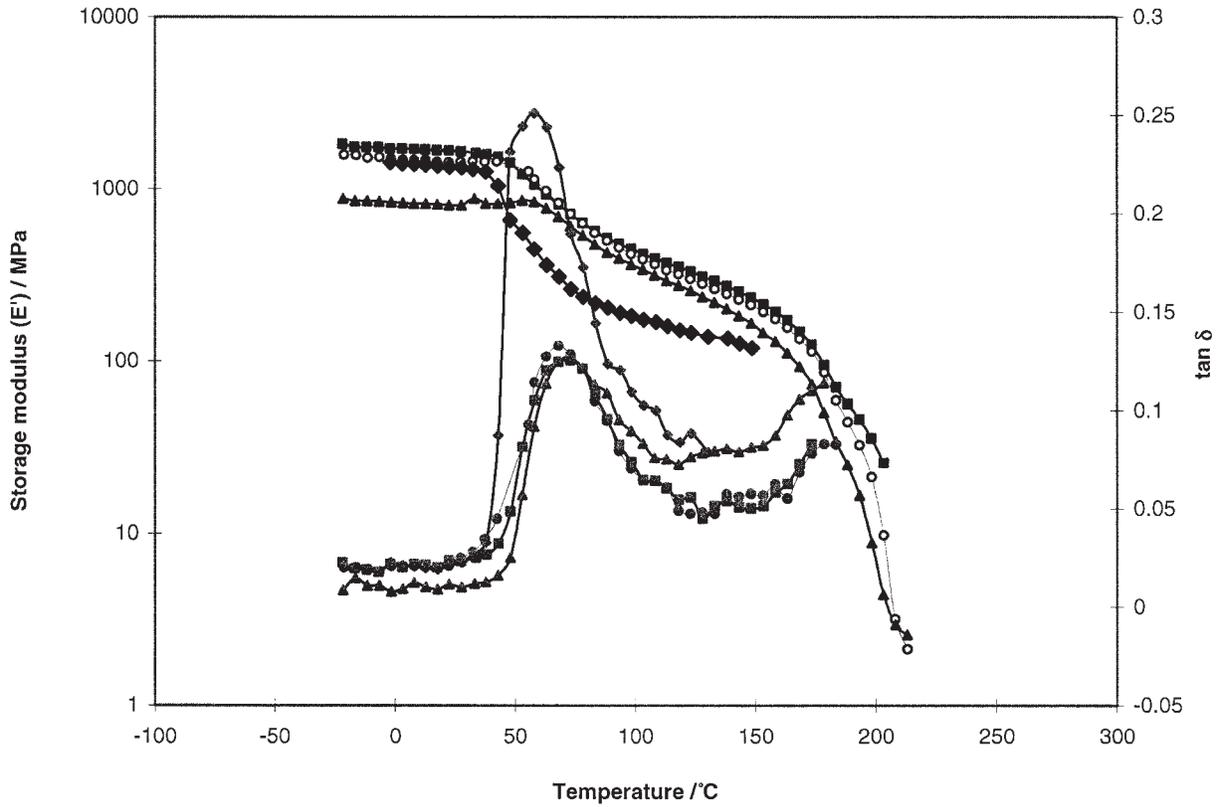


Figure 5 Comparisons of storage modulus (E') and $\tan \delta$ at 0.05% strain and 1.5 Hz for PBT film before and after irradiation with different doses (\blacklozenge , E' (0 Mrad); \blacksquare , E' (50 Mrad); \circ , E' (100 Mrad); \blacktriangle , E' (150 Mrad); \blacklozenge , $\tan \delta$ (0 Mrad); \blacksquare , $\tan \delta$ (50 Mrad); \circ , $\tan \delta$ (100 Mrad); and \blacktriangle , $\tan \delta$ (150 Mrad)).

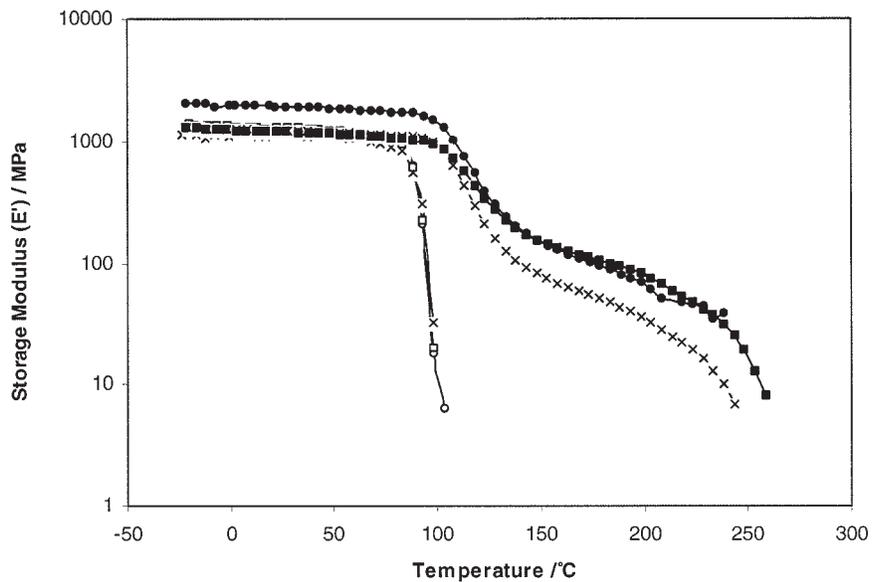


Figure 6 Comparisons of storage modulus (E') at 0.05% strain and 1.5 Hz for PCDT film with different thickness before and after irradiation (75 Mrad) (\circ , E' (0.06 mm, 0 Mrad); \times , E' (0.10 mm, 0 Mrad); \bullet , E' (0.20 mm, 0 Mrad); \bullet , E' (0.06 mm, 75 Mrad); \times , E' (0.10 mm, 75 Mrad); and \blacksquare , E' (0.20 mm, 75 Mrad)).

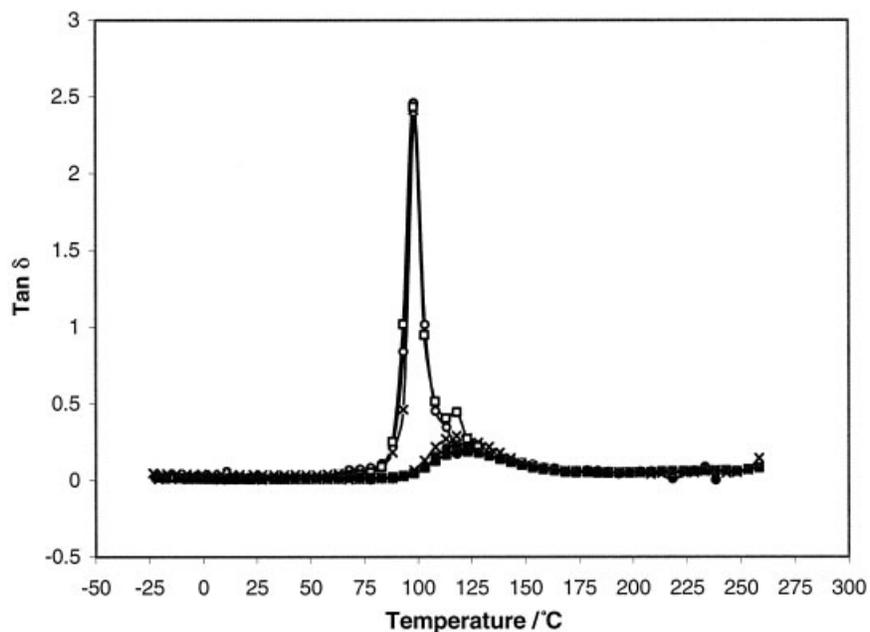


Figure 7 Comparisons of $\tan \delta$ at 0.05% strain and 1.5 Hz for PCDT film with different thickness before and after irradiation (75 Mrad) (○, E' (0.06 mm, 0 Mrad); ×, E' (0.10 mm, 0 Mrad); •, E' (0.20 mm, 0 Mrad); ●, E' (0.06 mm, 75 Mrad); ×, E' (0.10 mm, 75 Mrad); and ■, E' (0.20 mm, 75 Mrad)).

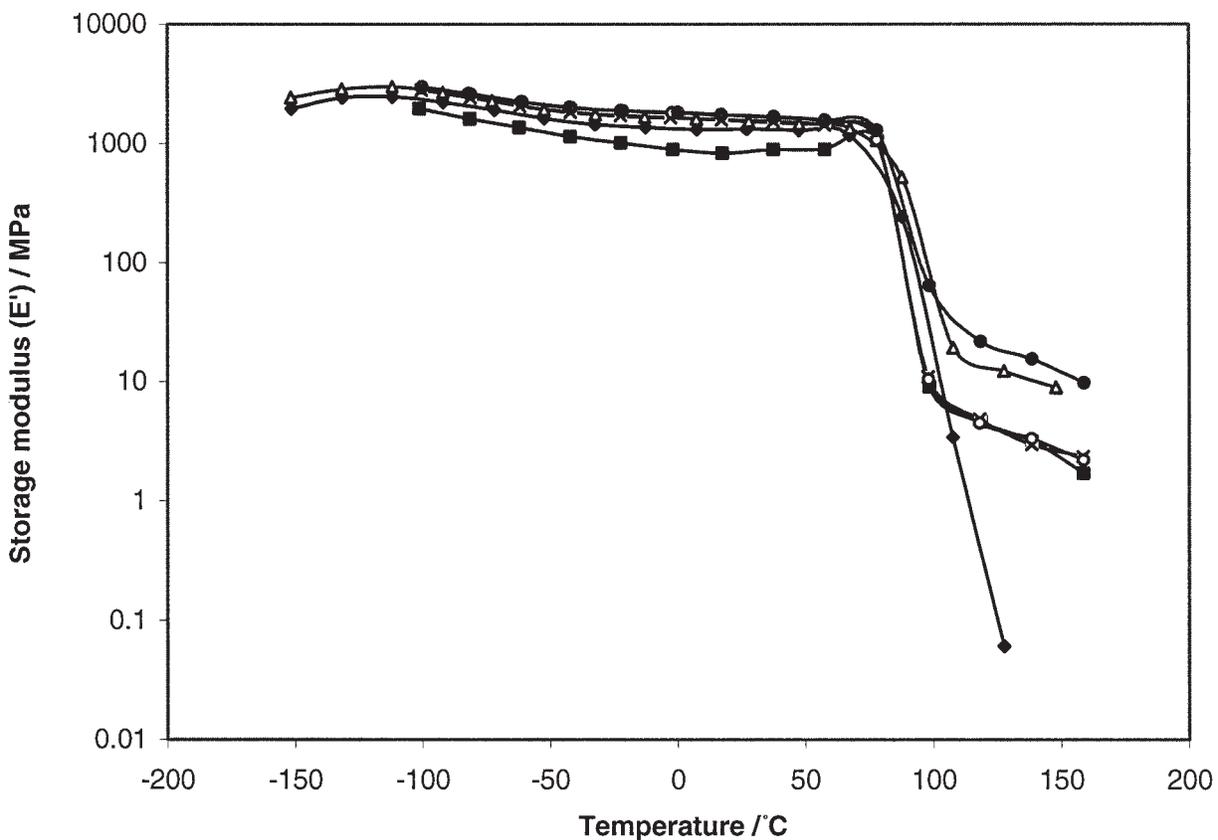


Figure 8 Comparisons of storage modulus (E') at 0.05% strain and 1.5 Hz for P(CDT-co-ET) 29 wt % ET films before and after irradiation with various doses (◆, E' (0 Mrad); ■, E' (25 Mrad); ×, E' (50 Mrad); Δ, E' (75 Mrad); ○, E' (125 Mrad); and ●, E' (150 Mrad)).

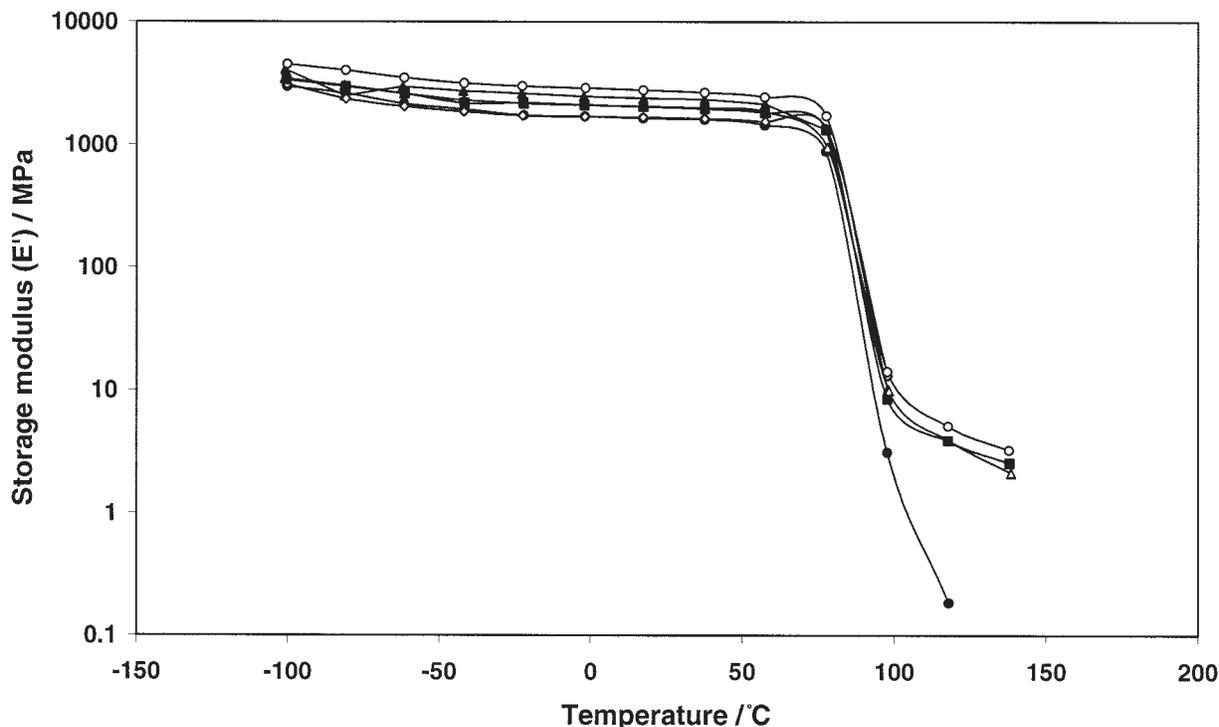


Figure 9 Comparisons of storage modulus (E') at 0.05% strain and 1.5 Hz for P(CDT-co-ET) 60 wt % ET films before and after irradiation with various doses (\blacklozenge , E' (0 Mrad); \times , E' (10 Mrad); Δ , E' (50 Mrad); \square , E' (75 Mrad); \blacksquare , E' (100 Mrad); and \circ , E' (150 Mrad)).

Melt rheology

The frequency dependence of the dynamic moduli, G' (in-phase, storage), and G'' (quadrature, loss), and shear complex intrinsic viscosity (η^*), from the nonirradiated and irradiated PBT films of increasing radiation doses are shown in Figure 10. The measurements were made soon after loading the samples in the rheometer to avoid degradation effects, although the films were found to be reasonably stable, undergoing only slight degradation after 1 h at the melt temperature in a nitrogen atmosphere. The nonirradiated PBT film was observed to behave as a viscous liquid, as shown in Figure 10(a). At frequencies less than 0.5 rad/s, the mechanical spectrum is indicative of a broad molecular weight distribution and with a molecular weight below the critical molecular weight for entanglement coupling (i.e., no rubbery plateau, nor a crossing of G' and G'').¹⁵ For the PBT films irradiated at various doses [Figs. 10(b)–10(e)], the initial frequency sweep shows elasticity dominant behavior, due either to partial crosslinking already existing, or to residual crystallinity at this temperature. When crosslinking occurs, G' and G'' increase with time as the network develops, and at a particular point, G' and G'' cross. The crossing of the G' and the G'' will be shifted to lower frequencies, if the polymers are highly crosslinked. Hence, it can be concluded that a considerable degree of crosslinking had been achieved in the PBT film.

To demonstrate more fully the progressive effect of increasing radiation dose, G' and G'' are replotted as a function of frequency in Figures 11 and 12, respectively. It can be seen that G' and G'' for the irradiated PBT films were higher than those for the nonirradiated PBT film at all frequencies and at all doses. As G' is associated with an index of melt elasticity, the results imply that the elasticity is enhanced after irradiation with various doses.¹⁶ G' and G'' of the irradiated PBT films increased with the irradiated dose of 24.7 Mrad, but decreased with further increases in dose. In both cases, G' and G'' showed maximum values at the dose of 24.7 Mrad. This probably results from simultaneous crosslinking and scission processes, both of which are now known to occur. It appears from the results that optimum crosslinking is achieved at the lower dose, and therefore, G' and G'' drop as β -bond scission is increased in the crystallites during irradiation and annealing below the melt.

The effect of irradiation on the relaxation modulus ($G(t)$) of the nonirradiated and irradiated PBT samples can be seen in Figure 13. For the nonirradiated sample, $G(t)$ relaxes steadily on the log–log scale, falling to a negligible quantity at the limit of reliable measurement of the instrument in about 1 s. All the irradiated samples, on the other hand, can be seen to have relaxed slowly until somewhere between 1×10^2 and 1×10^3 s plateaus were reached. Since the experiments are carried out in the melt, these plateau moduli rep-

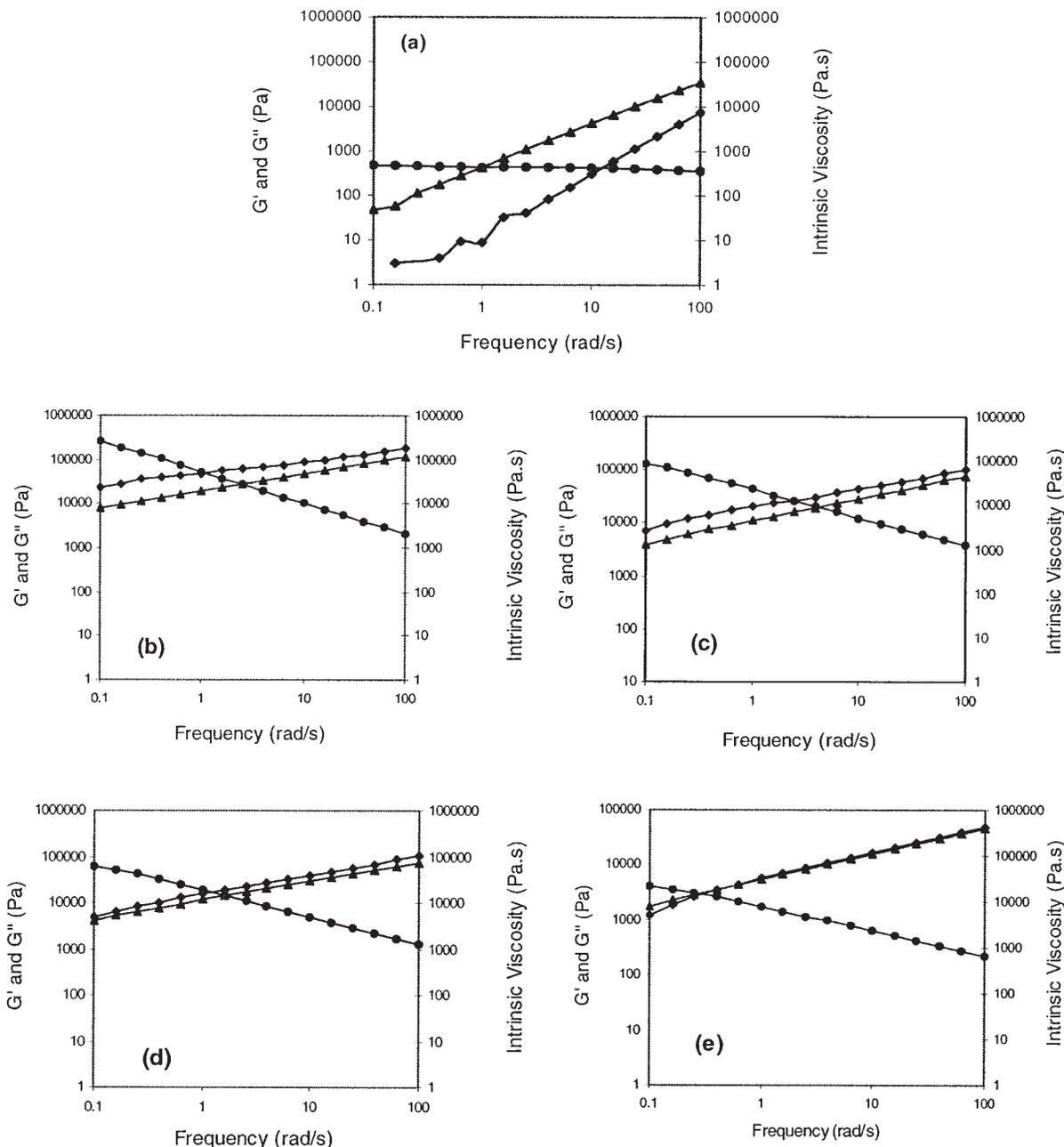


Figure 10 Frequency dependence of storage ($G' = \blacklozenge$), loss ($G'' = \blacktriangle$) moduli and dynamic viscosity ($\eta^* = \bullet$) for PBT films (a) 0 Gy, (b) 24.7 Gy, (c) 38.4 Gy, (d) 60.7 Gy, and (e) 114.6 Gy.

resent more truly the crosslink modulus free from entanglements and crystalline entrapments. As for the dynamic frequency sweep plots of G' and G'' described earlier and probably for the same reasons, the highest $G(t)$ and $G(t)_{lim}$ values occurred for the 24.7 Mrad dose sample. Thereafter, the $G(t)$ values diminished a little with increasing dose. Additionally, it may be that higher degrees of crosslinking cause loss of sensitivity in the measurement of angular displacement in the instrument.

However, gel fractions were not obtained at all for this highly crystalline ($\sim 41.1\%$) sample of PBT, and it

can only be concluded that the majority of the crosslinks were formed during the onset of the melt in the instrument prior to measurement. This is probably because radicals, either generated initially or resulting from β -bond scission, are free for the first time to crosslink in the oxygen-free melt situation of the rheometer. The rheology results indicate that, although a high degree of crosslinking was observed in the PBT films, it was induced at the stage of melt measurement and not during the experiment. This suggests that the maximum benefit from radiation-induced crosslinking of highly crystalline polyesters can only be achieved

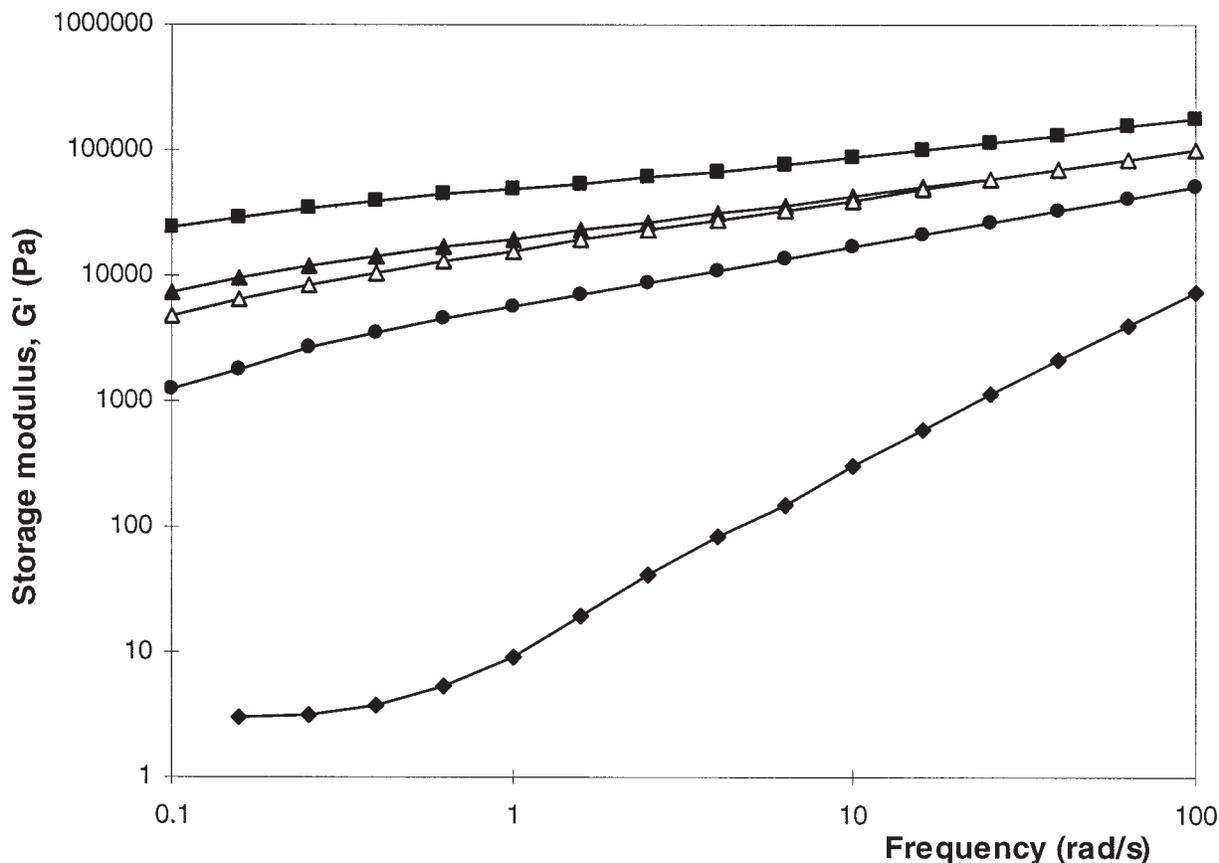


Figure 11 Storage moduli (G') as a function of frequency at 230°C, 1.5 mm thickness, and 10% strain for PBT film irradiated with different doses (\blacklozenge , 0 Mrad; \blacksquare , 24.7 Mrad; \blacktriangle , 38.4 Mrad; \triangle , 60.7 Mrad; and \bullet , 114.6 Mrad).

from oxygen-free, post-irradiation melt-annealing. More importantly, it demonstrates further, that the high degree of crystallinity of the PBT samples prevented reasonable levels of crosslinking being achieved below the melt.

Crosslinking was observed in compacted PCDT films by melt rheology, as shown in Figure 14, where $G(t)$ had relaxed to a limiting plateau value ($G(t)_{lim}$), which was apparently free from entanglement constraint. For the control, $G(t)$ relaxed steadily on the log-log scale, falling to a negligible value at the limit of reliable measurement of the instrument. For the doses of 8 and 17 Mrad, the stress relaxed more slowly following the stepped strain, and this reflects the increases in crosslinked network formation. Somewhere around 70 s after the stepped strain, the 8 Mrad sample reached a constant plateau value. However, the 17 Mrad sample did not reach a plateau. It appears, therefore, that degradation occurred during measurement. The PCDT had a lower degree of crystallinity ($\sim 32.1\%$) than that of the PBT film; hence, here also, some of the crosslinking may have been achieved during the melt measurements. However, the melt crosslink contribution is likely to have been much lower because, in addition to the lower crystallinity, it

is quite apparent that, under these conditions, main chain degradation was favored. It can be concluded that, in this case, a significant yield of crosslinking was achieved from below the melt annealing.

CONCLUSIONS

Enhanced levels of crosslinking in PET, PBT, PCDT, and P(CDT-co-ET) with 29 and 60% ET were observed by gel fraction measurements, high temperature storage moduli (G'), glass-transition temperature (T_g) increases, and retention of melt plateau relaxation moduli $G(t)_{lim}$, when samples of high molecular weight polyesters were irradiated and annealed in the presence of acetylene. This study generally showed improved ratios of crosslinking to scission with the combined use of (1) acetylene impregnation, (2) increasing the aliphatic glycol chain length, from PET through PBT to PCDT, and (3) reducing the proportion of crystallinity in the polyesters. Increasing the length of the alkyl linkage of the glycol moiety in the polyesters had the effect of reducing the fraction of available hydrogen atoms that could lead to β -bond scission. This confirms the observations made in our previous study.⁵ Reducing the proportion of crystallinity in the

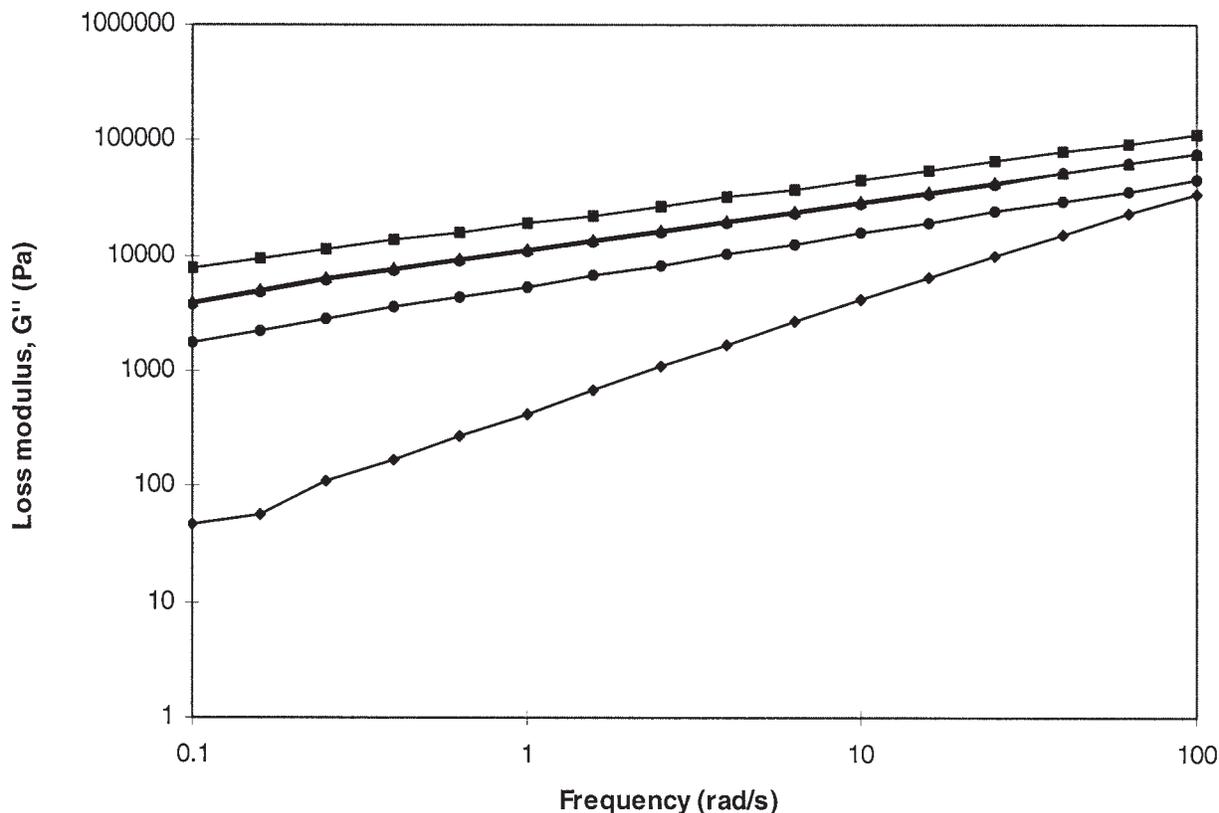


Figure 12 Loss moduli (G'') as a function of frequency at 230°C, 1.5 mm thickness, and 10% strain for PBT film irradiated with different doses (\blacklozenge , 0 Mrad; \blacksquare , 24.7 Mrad; \circ , 38.4 Mrad; \blacktriangle , 60.7 Mrad; and \bullet , 114.6 Mrad).

polyesters also gives rise to improved enhancement of crosslinking, in conjunction with acetylene impregnation and irradiation. It appears that, as long as crystallization is inhibited, high levels of crosslinking can be achieved in the polyesters by the use of acetylene. Reduction in crystallinity was also observed in going from thicker films to thinner films and fibers. The thicker films generally possessed higher degree of crystallinity due to slower cooling, when they were first prepared. Since the crystallites are unprotected from β -bond scission, reduction in the degree of crystallinity increases acetylene penetration and reduces the degree of main chain scission.

The crystalline melting temperature and degree of crystallinity in the polyesters were both observed by DSC measurements to decrease following irradiation. This was particularly noticeable in the highly crystalline PET and PBT polyesters. Since acetylene does not penetrate the polymer crystallites, and therefore, does not protect them from main chain β -bond scission, they are left completely open to radiation degradation. Acetylene enhanced crosslinking and scission reduction takes place only in the amorphous regions and at the amorphous-crystalline interfaces.

Enhanced crosslinking of polyesters was observed by DMTA, as a positive shift in the glass transition temperature (T_g), an increase in storage modulus (E'),

and a decrease in the loss tangent ($\tan \delta$) peak height, of PCDT and P(CDT-co-ET) films in the rubbery plateau region. Crosslinking was observed in compacted PCDT films by a melt rheology, where the relaxation moduli ($G(t)$) had relaxed to a limiting plateau value ($G(t_{lim})$), which was free from entanglements constraint. Unfortunately, degradation of the polyester also took place in the rheometer, at the melt temperatures required for measurement, and the levels of crosslinking could not be reliably evaluated. After a limiting dose, the storage modulus (G'), from frequency measurements of irradiated samples, became greater than the loss modulus (G''), over the whole frequency range. This is also strongly indicative of high levels of crosslinking, despite the degradation of the compacted PCDT in the rheometer. For PBT, crystallite-trapped radicals became melt-annealed in the rheometer, increasing $G(t_{lim})$ and therefore the number of crosslinks, far beyond the levels achievable by annealing below the melt.

The results presented here, together with those of the previous study,⁵ indicate that there are two sets of competing linear chain reactions following the radiation of acetylene-impregnated polyesters. Firstly, main chain β -bond scission initiated by alkyl radicals subjacent to the ester-glycol oxygen linkage and non-branching or linear, chain-reactions sustain the replen-

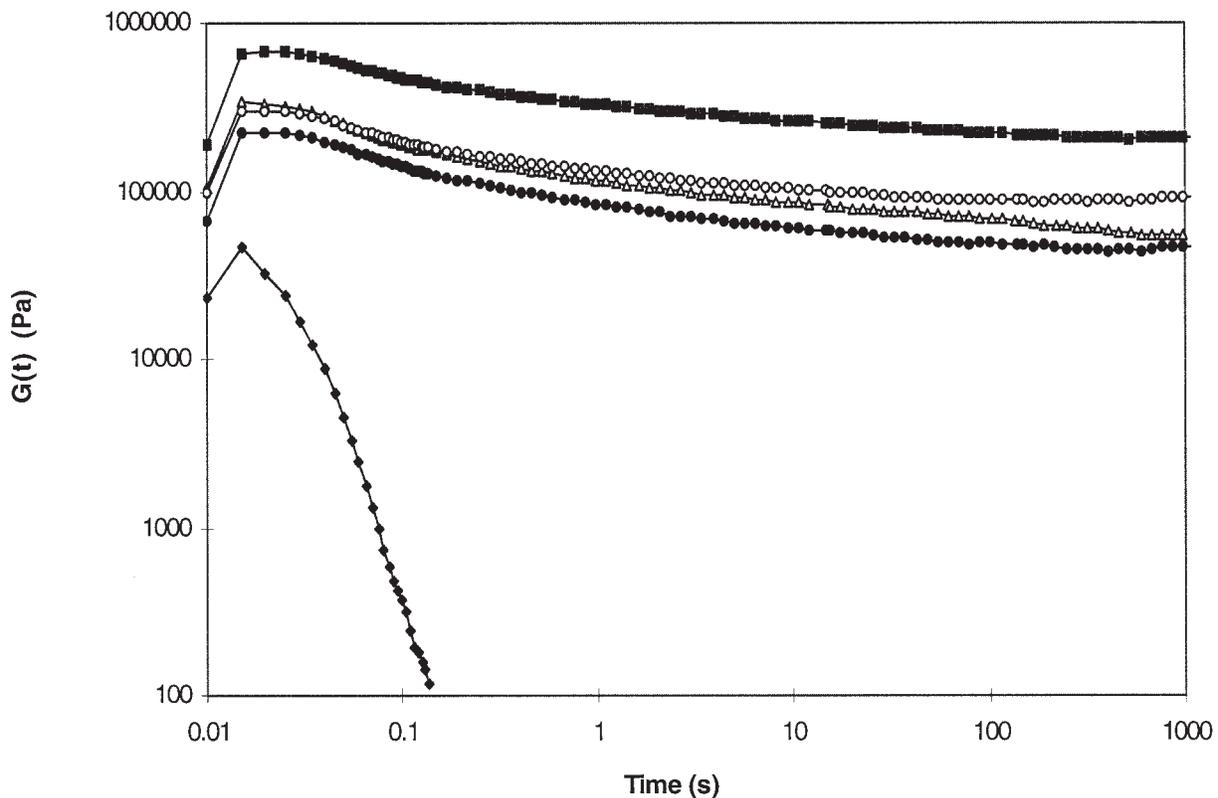


Figure 13 The relaxation moduli ($G(t)$) versus time (t) at 230°C, 1.5 mm thickness (five layers), and 2% strain for PBT irradiated with different doses (\blacklozenge , 0 Mrad; \blacksquare , 24.7 Mrad; \blacktriangle , 38.4 Mrad; \circ , 60.7 Mrad; and \bullet , 114.6 Mrad).

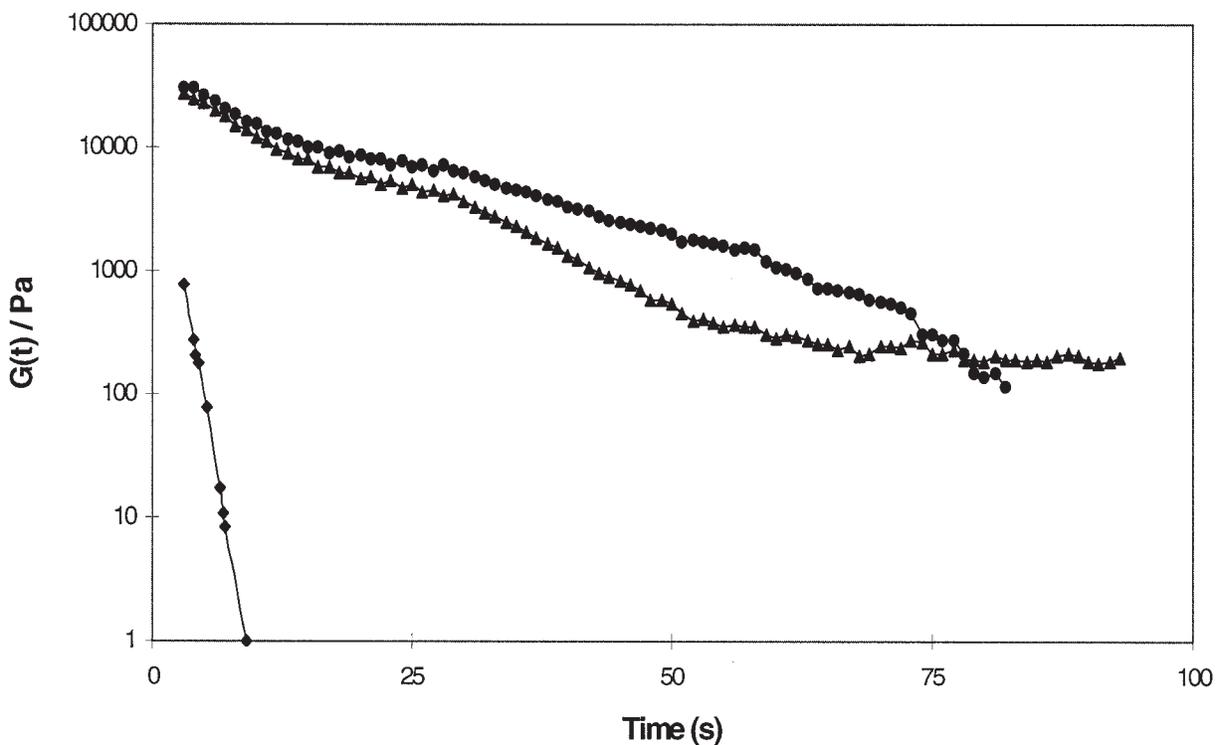


Figure 14 The relaxation moduli ($G(t)$) versus time (t) for PCDT films at 290°C after loading samples, 1.5 mm thickness (100 layers) at 2% strain (\blacklozenge , 0 Mrad; \blacktriangle , 8 Mrad; and \bullet , 17 Mrad).

ishment of these radicals by hydrogen atom abstraction reactions, particularly those of the carboxyl radical and the aromatic radical. Secondly, free-radical addition to acetylene, which eventually results in crosslinking via hydrogen atom abstraction, further free-radical unsaturated addition reactions between newly formed side chain adducts, and termination reactions. The addition of acetylene to the alkyl radical, by implication, inhibits β -bond scission, and the data in this article support the hypothesis.

Acetylene-enhanced crosslinking has been clearly demonstrated in polyesters and copolyesters, despite the difficulty of having to take measurements at high rubbery and melt temperatures, where polyesters are renown for their instability and tendency to depolymerize and degrade. Clearly, the degree of enhanced crosslinking was increased by increasing the length of the alkyl moiety. There is a limit to the usefulness of this approach and the length of alkyl moiety that can be introduced because, as the length of the alkyl moiety is increased, the polymer becomes more like the alkyl polymer, and therefore, has a reduced melting point and less of the more useful properties of a polyester. However, decreasing the degree of crystallinity of the polyesters by adding copolymers also increased the degree of crosslinking dramatically and reduced the level of β -bond scission by increasing the extent of acetylene protection. This could also prove to be an extremely useful technique. However, it must be remembered that many of the desired properties of ordinary polyesters arise from the crystalline-entrapped entanglements (CEE), which give rise to highly stable temporary crosslinks. It may be because extended crosslinking of the amorphous copolyesters could replace these CEEs and result in copolymers having the characteristics of truly crosslinked systems, but also

with some of the desired characteristics of the ordinary CEE polyesters.

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