

Electron Beam Crosslinking of Rigid-Rod Polyesters with Flexible Aliphatic Side Chains

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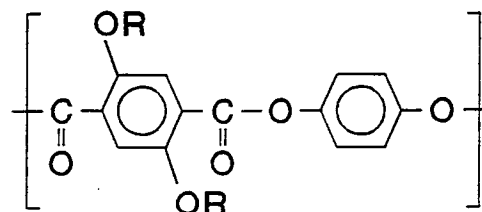
SYNOPSIS

The crosslinking of a series of thermotropic LC polyesters, consisting of a poly(*p*-phenylene terephthalate) backbone and flexible aliphatic side chains, by electron beam irradiation was studied as a function of the side-chain composition, side-chain length, and irradiation temperature. For a comparison of the effect of irradiation the $G(S)/G(X)$ ratio, as determined from sol-gel or GPC measurements, was used. Crosslinking dominates if this value is smaller than 1, which is the case for four out of five polyesters studied. Only the polyester with hexyloxy side chains shows a slight tendency to degradation. Crosslinking is stimulated by longer side chains and the introduction of hetero atoms that are more easily ionizable, like oxygen. The introduction of an unsaturation has the largest effect and boosts the crosslinking process. Raising the irradiation temperature increases the tendency to crosslinking or degradation already present. For most of the polyesters studied, irradiation slightly improves the mechanical properties of cast films. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The development of melt-processable liquid crystalline polymers has received a great deal of attention in the recent years and was triggered by the high mechanical properties of fibers spun from shear oriented lyotropic aramid solutions.¹ Melt processability of a rigid-rod polymer is usually attained by disrupting the regular structure of the rigid main chain by means of random copolymerization and/or the introduction of crankshafts² or flexible spacers.³ The result of this is a frustrated chain packing that lowers the melting point. Most commercial LCPs are based on these principles. Another possibility is the introduction of flexible side chains onto the rigid aromatic backbone. Substitution of the aromatic units not only suppresses the melting point, it also improves the solubility of these polymers in common solvents.⁴⁻⁸ Some of these polymers exhibit novel types of mesophases.⁶⁻⁸ The phase behavior,^{9,10} structure,¹¹ spinning,¹² and mechanical properties¹³ of this class of TLCPs have been extensively studied at our laboratories.

Processing from the LC melt induces macroscopic orientation, which is retained on solidification, yielding products with exceptional mechanical properties in the direction of orientation as well as high levels of anisotropy. Disadvantages of the large anisotropy in mechanical properties and the low cohesive forces between the aligned polymeric chains are the susceptibility to fibrillation and, in the case of fibers, a low compressive strength. One approach to improve these (off-axis) properties is crosslinking.¹⁴⁻¹⁷ Crosslinking of TLCPs in general requires the introduction of functional groups. Olefinic groups are used most frequently to this end, and these can be crosslinked by thermal,¹⁸⁻²⁰ chemical,²¹ or UV irradiation^{15,22} methods.



| | |
|------|--------------------------------------------------------------------------------------------|
| C6 | : R = -(CH ₂) ₅ -CH ₃ |
| C6O | : R = -(CH ₂) ₃ -O-CH ₂ -CH ₃ |
| C6= | : R = -(CH ₂) ₄ -CH=CH ₂ |
| C12 | : R = -(CH ₂) ₁₁ -CH ₃ |
| C12O | : R = -(CH ₂) ₆ -O-(CH ₂) ₄ -CH ₃ |

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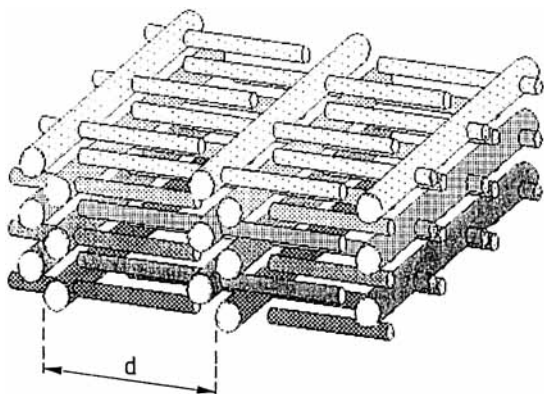


Figure 1 Schematic representation of the layered solid-state structure of poly(*p*-phenylene 2,5-dialkoxyterephthalate)s and poly(*p*-phenylene 2,5-di(alkoxyalkoxy)terephthalate)s; the main chains are separated by the interdigitating side chains (for details, see references 10 and 11)

In this article we report on the efficiency of electron beam (EB) crosslinking of rigid-rod polyesters with flexible aliphatic side chains using the LCPs displayed in Scheme 1. The aliphatic side chains may be regarded as functional groups for electron beam irradiation. Evidence hereto can be derived from the work of Cai et al.,²³ who investigated the use of poly(octyl thiophene) as electron beam resists. These poly(alkyl thiophene)s have a solid-state structure that resembles that of our LC polyesters.²⁴ In both systems, the flexible side chains interdigitate to form main chain layers^{7,9-13,24} (see, for example, Fig. 1). The driving force for this layered organization is the unfavorable interaction between the polar main chains and the apolar side chains (analogous to microphase separation in block copolymers). Exposure to accelerated electrons renders the poly(octyl-thiophene) films insoluble.²³ The crosslinked polymer retained the electrical conductivity of the original polymer. This observation suggests that crosslinking occurred via the octyl side chains rather than the thiophene rings.

Based on evidence gathered on more common polymers as polyethylene, polypropylene, polyoxymethylene, polybutadiene,²⁵ and a series of poly(*n*-methacrylates),²⁶ it is expected that both the composition and the length of the side chains may strongly influence the crosslinking efficiency in this class of materials and, thus, the mechanical properties. These aspects have been extensively studied by measuring the ratio of the radiochemical yields of chain scission and crosslinking ($G(S)/G(X)$) and the mechanical properties of irradiated and unirradiated cast films, the results of which are reported herein.

EXPERIMENTAL

Materials

The poly(*p*-phenylene 2,5-dialkoxyterephthalate)s **C6** and **C12** and the poly(*p*-phenylene 2,5-di(alkoxyalkoxy)terephthalate)s **C60** and **C120** used in this study (see Scheme 1) were prepared by solution polycondensation as described previously.^{9,10} Poly(*p*-phenylene-2,5-dihexyloxyterephthalate) **C6=** was synthesized in a manner analogous to poly(*p*-phenylene-2,5-dihexyloxyterephthalate) **C6**⁹, except that 1-bromo-6-hexene was used instead of 1-bromohexane. The inherent viscosities (chloroform, 2 g/L, 25°C) and the molar mass, as determined by GPC against polystyrene (PS) standards, are given in Table I. Only for the **C6** polyester the Mark-Houwink relationship is known, allowing the calculation of the true weight average molar mass from the molar mass according to PS calibration.²⁷ The Mark-Houwink constants for the **C6** polyesters²⁸ and PS²⁹ in chloroform at 25°C are $K = 3.08 \times 10^{-3}$, $a = 0.97$, and $K = 7.16 \times 10^{-3}$, $a = 0.76$, respectively. For the **C6** polymer, a weight average molar mass of 39000 g/mol is, thus, calculated. Its number average molar mass amounts to 15,600, corresponding to an average of 35 repeating units per chain.

Isotropic films were obtained by casting a chloroform solution (4–6 wt %) onto a glass plate. After evaporating the solvent, thin films were obtained with a rather uniform thickness of approximately 40 μm . Contrary to the other films, the as-cast **C12** films have a highly crystalline structure.⁹⁻¹⁴ To facilitate the crosslinking process, these **C12** films were heated to 120°C and subsequently quenched to room temperature, which renders a less crystalline structure.^{11,13}

Electron Beam Irradiation

Electron beam irradiation was carried out at room temperature and at 120°C under a nitrogen atmo-

Table I Inherent Viscosities and Molar Mass Distribution of the Synthesized Polymers

| Polymer | $\eta_{\text{inh}}^{\text{a}}$ (dL/g) | M_w^{b} | M_w/M_n^{b} |
|---------|------------------------------------------|------------------|----------------------|
| C6 | 1.77 | 85300 | 2.5 |
| C60 | 1.65 | 111000 | 5.8 |
| C6= | 2.52 | 74700 | 3.8 |
| C12 | 3.10 | 222000 | 2.4 |
| C120 | 2.85 | 299000 | 5.2 |

^a Determined at 25°C in CHCl_3 (2 g/L).

^b From GPC against polystyrene standards.

sphere, using a 175 kV electron curtain EB system (ESI, model CB 150/15/180 L). The doses delivered were calculated according to:

$$D = k(I/v)$$

with v is the conveyer belt speed [meter per minute (mpm)], I the current (mA), and k the yield value as determined by Far West radiochromic dosimeters [$k = 20.2 \pm 1.0$ (Mrad mpm)/mA at 95% confidence level]. The voltage was set at 175 kV to ensure a homogeneous irradiation over the thickness of the sample. The samples were irradiated with doses up to 175 MRad in six discrete steps, i.e., 10, 40/45, 60, 90, 120, and 175 MRad. As the maximum obtainable dose in one run amounted to 30 MRad, sequential runs were needed to obtain the higher doses. The samples were mounted on a massive brass plate. For high-temperature measurements, the brass plate was preheated to 120°C. Due to the small thickness of the LCP films, this temperature is adopted within 20 s after placing the films onto the brass plate, as checked with IR temperature measurements. The whole experiment, from placing the LCP films on the preheated copper plate to performing the EB irradiation, took less than 1 min. The temperature during EB irradiation was stable within 5°C.

Characterization Methods

The gel fraction was determined by soxhlett extraction. About 25 mg of an irradiated polymer sample was extracted with chloroform until all soluble material was removed. This usually took about 8–12 h, and was followed by drying at room temperature for 24 h. The weight of the samples before and after extraction was measured after conditioning for 24 h at 23°C and 50% relative humidity (RH) in a dark room. The values given are the averages of at least five measurements.

Gel permeation chromatography (GPC) was run on a Waters GPC-1, using Ultrastayragel columns of 100, 1000, and 10,000 nm in conjunction with a UV detector and a differential refractometer (eluent: chloroform, flow rate: 1 mL/min, column temperature 40°C).

The mechanical properties of the films before and after irradiation were determined by tensile tests, performed on a small tensile testing machine. The samples were stored for at least 48 h in a conditioned room (23°C, 50% RH) prior to the testing. The strain rate was 10%/min. Initial cross-sectional areas, used for calculating the Young's modulus and tensile strength, were obtained from the mass, length, and

density of the films. The values given are the averages of at least six measurements.

RESULTS AND DISCUSSION

Crosslinking/Degradation

Electron beam (EB) irradiation of a polymeric material generates radicals that lead to both chain scission and crosslinking processes. The relative occurrence of these processes is determined by the chemical composition.²⁵ The macroscopic effect of EB irradiation depends among others on the initial molar mass.^{30,31} To evaluate the effect of side-chain composition and side-chain length on the crosslinking process, the influence of the initial molar mass has to be discarded. This can be done by comparing the $G(S)$ and $G(X)$ values, which give the number of main-chain scissions and the number of crosslinks produced per 100 eV of absorbed energy.

Formally, the two processes, i.e., chain scission and crosslinking, occur simultaneously. However, Charlesby argued that these processes may be viewed as occurring consecutively due to the random nature of the two processes.³⁰ In the first step, chain scission takes place and results in a modified molecular mass distribution. The second step consists of crosslinking this new distribution. In the particular case of a Flory distribution, the resulting distribution after chain scission is again of the Flory type but with a new weight average molar mass.³⁰ The crosslinking of such Flory distributions and the relation between the irradiation dose and the sol fraction has been theoretically described by Charlesby.³¹ Going one step further, Charlesby and Pinner³² combined the effects of consecutive chain scission and crosslinking on a Flory distribution and derived the following relation between the radiochemical yields of crosslinking ($G(X)$) and chain scission ($G(S)$) and a measurable quantity as the sol fraction (S):

$$S + S^{1/2} = \frac{9.615 \times 10^2}{DM_{no}G(X)} + \frac{G(S)}{G(X)} \quad (1)$$

where D is the dose in Mrad and M_{no} is the initial number average molar mass of the polymer in kg/mol. The value of $G(X)$ can be derived from the slope of a $S+S^{1/2}$ plot against $1/\text{dose}$ if the number average molar mass is known. The value of $G(S)/G(X)$ follows from the intercept.

The molar mass distribution of polyesters and polyamides can generally be described by a Schultz–Zimm distribution and often even with a Flory distribution,³³ which presents a special case of the

Schultz-Zimm distribution, i.e., $M_w/M_n = 2$. Clearly, the LC polyesters synthesized do not comply with a Flory distribution. It was, however, assumed that they could be described with a Schultz-Zimm distribution. Kotliar^{34,35} showed that random chain scission of a Schultz-Zimm distribution again yields a Schultz-Zimm distribution with a new width (M_w/M_n) parameter, which very rapidly approaches the Flory value of 2. For modeling purposes we, therefore, assumed that our Schultz-Zimm distributions are converted to Flory distributions, which are subsequently crosslinked. It can be shown that, under these assumptions, the relationship between the radiochemical yields of crosslinking and degradation and the sol fraction is similar to the one previously derived for Flory distributions [eq. (1)].

Unfortunately, the Mark-Houwink constants of the LC polyesters used are not known, with the exception of the C6 polyester. This prevents the calculation of the actual weight and number average molar masses from the GPC data against PS standards.²⁷ As a result, only the ratio $G(S)/G(X)$ can be determined and will be used to compare the effect of side-chain composition and side-chain length on the crosslinking of rigid rod polyesters with flexible aliphatic side chains in the following discussion.

The soluble fractions after irradiation of the various LC polyesters are collected in Table II. For the C6 polyester, a gel is only found when irradiated at 120°C with a high dose of 175 Mrad. This prohibits the determination of the $G(S)/G(X)$ value according to eq. (1). However, as the Mark-Houwink constants for the C6 polyester are known,²⁸ the actual molecular weight can be determined by GPC,²⁷ allowing the calculation of the $G(S)/G(X)$ value from the following set of equations^{36,37} (with $(c + 1)/c = M_w/M_n$):

$$\frac{1}{M_n} = \frac{1}{M_{no}} + 1.04 \times 10^{-3} D \left[G(S) - \frac{G(X)}{2} \right] \quad (2)$$

$$\frac{1}{M_w} = \frac{1}{M_{wo}} + 1.04 \times 10^{-3} D \left[\frac{c+2}{3(c+1)} G(S) - G(X) \right] \quad (3)$$

M_n is the number average molar mass after irradiation. M_{wo} and M_w are the initial weight average molar mass and the weight average molar mass after irradiation. Formula 3 is only applicable when chain scission is not too much dominant. This is the case if:³⁷

Table II Soluble Fraction of the Irradiated Polymers

| Polymer | Dose (Mrad) | Soluble Fraction Irradiation Temperature | |
|---------|-------------|------------------------------------------|-------|
| | | 25°C | 120°C |
| C6 | 10 | 1.000 | 1.000 |
| | 40 | | 1.000 |
| | 45 | 1.000 | |
| | 60 | 1.000 | 1.000 |
| | 90 | 1.000 | 1.000 |
| | 120 | 1.000 | 1.000 |
| | 175 | 1.000 | 0.849 |
| C60 | 10 | 1.000 | 1.000 |
| | 40 | | 1.000 |
| | 45 | 1.000 | |
| | 60 | 1.000 | 0.879 |
| | 90 | 0.931 | 0.728 |
| | 120 | 0.791 | 0.646 |
| | 175 | 0.629 | 0.524 |
| C6= | 10 | 0.960 | 0.847 |
| | 20 | 0.445 | 0.372 |
| | 40 | | 0.163 |
| | 45 | 0.175 | |
| | 60 | 0.132 | 0.104 |
| | 90 | 0.085 | 0.064 |
| | 120 | 0.065 | 0.048 |
| C12 | 175 | 0.047 | 0.034 |
| | 10 | 1.000 | 1.000 |
| | 40 | | 0.683 |
| | 45 | 0.657 | |
| | 60 | 0.539 | 0.440 |
| | 90 | 0.411 | 0.305 |
| | 120 | 0.305 | 0.239 |
| C120 | 175 | 0.253 | 0.172 |
| | 10 | 1.000 | 1.000 |
| | 40 | | 0.437 |
| | 45 | 0.480 | |
| | 60 | 0.394 | 0.301 |
| | 90 | 0.292 | 0.198 |
| | 120 | 0.214 | 0.150 |
| | 175 | 0.168 | 0.091 |

$$\left[\frac{(c+2)(c-1)}{36c^2} \times \frac{G(S)}{G(X)} \right] \ll 1 \quad (4)$$

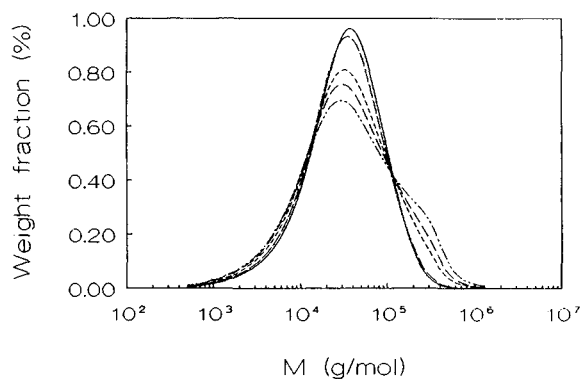
Table III shows the influence of irradiation on the number and weight average molar mass of the C6 polyester, based on GPC measurements before and after irradiation. The number average molar mass decreases with dose, whereas the weight average molar mass increases yielding a broader distribution. As can be inferred from the GPC curves (Fig. 2), the system as a whole tends towards a bi-

Table III Number and Weight Average Molar Mass of the C6 Polyester as a Function of Irradiation Dose

| Temperature (°C) | Dose (Mrad) | M_n (kg/mol) | M_w (kg/mol) |
|------------------|-------------|-------------------|-------------------|
| 25 | 0 | 16.2 | 40.3 |
| | 10 | 15.7 | 42.5 |
| | 60 | 15.2 | 51.6 |
| | 90 | 14.2 | 56.1 |
| | 120 | 13.8 | 66.9 |
| 120 | 175 | 12.8 | 75.6 |
| | 10 | 15.8 | 41.4 |
| | 60 | 15.0 | 54.5 |
| | 90 | 14.2 | 58.2 |
| | 120 | 13.5 | 63.0 |
| | 175 | 11.5 ^a | 56.9 ^a |

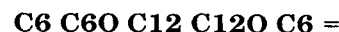
^a Soluble part, material does not dissolve completely.

modal distribution upon irradiation. The values of $G(S)$ and $G(X)$ can be derived from the slopes of the $1/M_n$ and $1/M_w$ plots against the dose (Fig. 3) and are displayed in Table IV, together with the calculated values [eq. (1)] for the other LC polyesters. For the C6 polyester, with $c = 0.67$, the left-hand side of formula 4 is much smaller than 1, proving the validity of using formula 3 for the determination of the $G(S)$ and $G(X)$ values. $G(S)/G(X)$ values somewhat larger than one are found for the C6 polyester, indicating that the system as a whole has a slight tendency for degradation. Despite the tendency to degradation, gelation occurs when these polyesters are irradiated at 120°C with a dose of 175 Mrad. GPC measurements showed that irradiation leads to a bimodal distribution, of which the high molar mass part is crosslinked with ongoing irradiation.

**Figure 2** GPC curves of unirradiated (—) and at room temperature-irradiated C6; 10 (---), 60 (.....), 90 (— · —), 120 (— · — · —), and 175 (· · · · ·) Mrad.**Table IV** Calculated $G(S)/G(X)$ Values

| Polymer | Irradiation Temperature (°C) | $G(S)/G(X)$ |
|---------|------------------------------|-------------|
| C6 | 25 | 1.07 |
| | 120 | 1.10 |
| C60 | 25 | 0.93 |
| | 120 | 0.99 |
| C6= | 25 | 0.17 |
| | 120 | 0.13 |
| C12 | 25 | 0.52 |
| | 120 | 0.33 |
| C120 | 25 | 0.39 |
| | 120 | 0.22 |

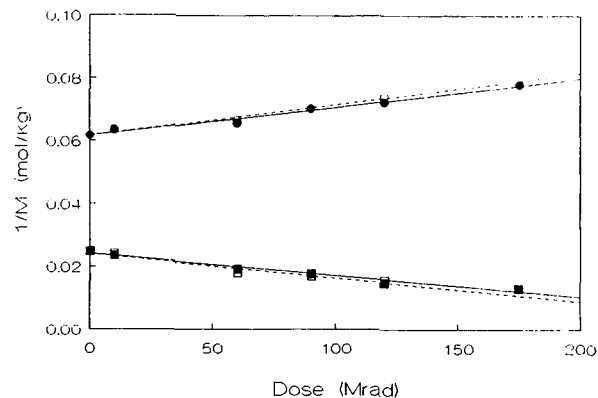
The exchange of a CH_2 group by oxygen shifts the $G(S)/G(X)$ ratio to a value just smaller than 1, indicating that these C60 polymers have a slight tendency for crosslinking. For the other three polymers in this study, crosslinking clearly prevails as can be inferred from the $G(S)/G(X)$ values, which are much smaller than 1. Based on the $G(S)/G(X)$ ratios, the following order can be derived for the investigated polymers with respect to crosslinking/degradation processes:



←degradation---|-----crosslinking-----→

Mechanism

It is well known that unsubstituted aromatic polyesters predominantly undergo chain scission when irradiated under vacuo or nitrogen.^{25,46} Compared with carbon-carbon bonds, the carbon-oxygen bond is less stable, and chain scission most likely occurs at the aryl-ester linkage, yielding an aryl radical.^{46,47}

**Figure 3** Reciprocal values of the molar mass vs. irradiation dose for the C6 polyester ●: M_n (25°C), ○: M_n (120°C), ■: M_w (25°C), □: M_w (120°C).

These as well as other radicals formed will react with oxygen when the samples are exposed to air, which is immediately after the irradiation under nitrogen. Besides acting as a radical scavenger, oxidation generally leads to further degradation.

The attachment of side chains facilitates the crosslinking in two ways. First of all, through recombination of radicals generated in two adjacent side chains belonging to different main chains. Cai et al.²³ presented some evidence that suggest that crosslinking in similar systems occurs in the side chain region. As recombination requires the radicals to come in close proximity of one another, earlier investigations with regard to the structure and molecular mobility are worth mentioning. X-Ray measurements show that the average distance between adjacent side chains in the typical interdigitated structure (which is preserved after irradiation)³⁸ is 4–7 Å.^{9–14,39} Other investigations show that for all investigated polymers a β -relaxation at around -35°C is present, which involves a cooperative motion of the side chains.^{40–44} Due to this mobility, the distance between the adjacent side chains may locally be much smaller than the average distance. It is believed that this mobility of the side chains together with the radical migration within the side chains⁴⁵ enhances the possibility for recombination, resulting in the crosslinking observed.

Secondly, the side chains will absorb part of the radiation. Consequently, the number of radicals generated in the main chain and the resulting degradation decrease. For a fixed dose, the energy absorbed by the main chains is proportional to the weight fraction of the main chains. In this way, an increase in side chain length will lower the degree of degradation of the main chains resulting in lower $G(\text{S})/G(\text{X})$ values, as was experimentally observed. Similar results were previously reported by Schultz et al.²⁶ for a series of *n*-alkylmethacrylates.

Replacing a CH_2 group by oxygen has a positive effect on the crosslinking process. It can be explained by the fact that oxygen is more easily ionizable than carbon. As a result, more radicals are generated upon the interaction with incident radiation, which implies that for a given dose, the number of radicals formed in the side chains will be raised when replacing a CH_2 group by oxygen. The effect is more pronounced for the LCPs with longer side chains. The introduction of an unsaturation has by far the most profound effect and boosts the crosslinking process, even at relatively low doses of irradiation. This is not surprising, as we are dealing with a propagation reaction rather than a recombination of radicals, as is the case for the other polymers in this study. Raising the EB-irradiation temperature

strengthens the tendency to crosslinking or degradation already present.

Comparison with Other Crosslinking Methods

The high efficiency of olefinic groups towards crosslinking has been used previously to crosslink shaped products like fibers of thermotropic polyesters thermally,^{18–20} chemically,²¹ or via UV irradiation.^{15,22} The described thermal and chemical crosslinking processes require prolonged reaction times (>3 h) before crosslinking is virtually complete. As a result of the absorbance of the incident UV light by the LCP, crosslinking is confined to the outer surface layers of the spun fibres ($d = 45 \mu\text{m}$), even though Lin et al.¹⁵ chose the wavelength of the incident UV light in the range where the polymer least absorbs the radiation. Compared to the above described UV and, particularly, the thermal- and chemical-induced crosslinking processes, EB irradiation is a much faster process. Densely crosslinked networks can be obtained in seconds. Furthermore, under the conditions used, EB irradiation ensures a homogeneous crosslinking over the thickness of the samples, up to a sample thickness of $\pm 100 \mu\text{m}$.

Mechanical Properties

A good insight in the effect of EB irradiation on the mechanical properties of isotropic films can be obtained by comparing the stress–strain curves rather than the absolute values for modulus and strength as displayed in Table V. Irradiation of the **C6** and **C60** polyesters only leads to small changes in the stress–strain behavior. This is schematically shown in Figure 4(a). Basically, the same stress–strain curve is followed. An increase in strain is found with increasing dose, resulting in somewhat higher strength values. Although degradation dominates for the **C6** polymer, some high molecular weight material is formed upon irradiation, leading to a bimodal molecular weight distribution. The increase in strain is thought to be related with this high molecular weight fraction. Minor modifications in the stress–strain curves are also found for the **C12** polyester. Despite the fact that this material predominantly crosslinks, irradiation leads to a more brittle material with accompanying lower mechanical properties [Fig. 4(b)].

Significant changes in the stress–strain curves are found for the **C120** and **C6=** polyester. With increasing crosslink density, the modulus of the **C6=** polyester increases, whereas the strength remains roughly the same. This implies an increasing brittleness of the material as exemplified by the de-

Table V Mechanical Properties of the Irradiated Films

| Polymer | Dose (Mrad) | Modulus (GPa) ^a | Tensile Strength (MPa) ^a | Breaking Strain (%) ^a |
|---------|-------------|----------------------------|-------------------------------------|----------------------------------|
| C6 | none | 2.61 (0.16) | 21.6 (2.1) | 1.2 (0.1) |
| | 60 | 2.63 (0.14) | 23.1 (2.6) | 1.2 (0.2) |
| | 90 | 2.77 (0.05) | 26.0 (3.9) | 1.4 (0.4) |
| | 120 | 2.90 (0.09) | 28.9 (1.7) | 1.5 (0.2) |
| | 175 | 2.89 (0.08) | 32.1 (1.9) | 2.3 (0.6) |
| C60 | none | 4.12 (0.21) | 55.1 (1.6) | 3.4 (0.4) |
| | 10 | 4.29 (0.12) | 57.9 (7.0) | 4.4 (2.2) |
| | 60 | 4.39 (0.11) | 60.1 (5.0) | 5.5 (1.7) |
| | 120 | 4.31 (0.09) | 63.0 (9.8) | 6.4 (3.1) |
| | 175 | 4.28 (0.07) | 64.9 (2.7) | 6.3 (0.7) |
| C6= | none | 2.66 (0.09) | 47.6 (1.1) | 24.2 (1.9) |
| | 10 | 2.71 (0.07) | 47.3 (2.8) | 16.9 (3.0) |
| | 60 | 2.82 (0.06) | 45.5 (4.5) | 4.8 (3.5) |
| | 120 | 2.85 (0.05) | 44.5 (2.5) | 3.2 (0.9) |
| | 175 | 2.98 (0.07) | 38.9 (5.7) | 1.8 (0.4) |
| C12 | none | 0.47 (0.04) | 31.5 (1.0) | 76.1 (17.3) |
| | 60 | 0.53 (0.03) | 26.4 (2.3) | 45.1 (4.9) |
| | 90 | 0.53 (0.02) | 26.6 (2.6) | 42.1 (10.7) |
| | 120 | 0.49 (0.03) | 22.4 (3.1) | 34.9 (5.6) |
| | 175 | 0.46 (0.01) | 17.4 (1.5) | 23.0 (3.0) |
| C120 | none | 0.21 (0.01) | 5.94 (0.17) | 25.5 (7.2) |
| | 10 | 0.22 (0.01) | 7.34 (0.43) | 38.2 (13.2) |
| | 60 | 0.23 (0.01) | 9.21 (0.63) | 66.0 (16.4) |
| | 90 | 0.22 (0.01) | 9.57 (0.54) | 56.3 (9.8) |
| | 120 | 0.23 (0.01) | 9.55 (0.53) | 54.4 (11.0) |
| | 175 | 0.22 (0.01) | 9.24 (0.74) | 39.2 (10.7) |

^a Standard deviation given in parentheses.

creasing strain [Fig. 4(c)]. Triggered by the unusual high breaking strain of the unirradiated **C6=** films (see Table V), some additional sol-gel measurements were performed after the mechanical testing. Not only has the unirradiated **C6=** film become partially insoluble, all irradiated **C6=** films show a higher degree of crosslinking than their counterparts used for the determination of the G(S)/G(X) ratios. Moreover, a perfect match with the previous sol-gel data could be obtained if an extra irradiation dose of 14 Mrad was assumed. The two groups of films have received the same treatment except that the films used for mechanical testing were stored for at least 48 h in a well-lit conditioned room prior to testing. It is well known that polyesters containing olefinic groups are susceptible to crosslinking upon UV irradiation.^{15,22} We, therefore, assume that the (weak) UV emission by the strip lighting present in the conditioned chamber caused the extra crosslinking. When the **C120** polyester is irradiated, the yield strength, ultimate breaking strength, and breaking strain increase up to a dose of 60 Mrad,

after which it remains constant. The modulus is not affected by the EB irradiation [Fig. 4(d)]. The effect of irradiation on the mechanical properties of the **C12** and **C120** polyesters differs markedly, despite the fact that in both cases a crosslinked network is formed. Although no proof can be given at present, we feel that this is related to the morphological differences between the **C12** and **C120** polyester films. Whereas the **C120** films are strictly isotropic,¹⁰ orthotropic behavior is found in the **C12** films¹³ with the main chains oriented parallel to the film surface and the side chains perpendicular hereto.

CONCLUSIONS

The experiments performed show that the introduction of aliphatic side chains onto a rigid rod aromatic polyester has a profound influence on the crosslink efficiency upon EB irradiation. Whereas unsubstituted aromatic polyesters mainly degrade,

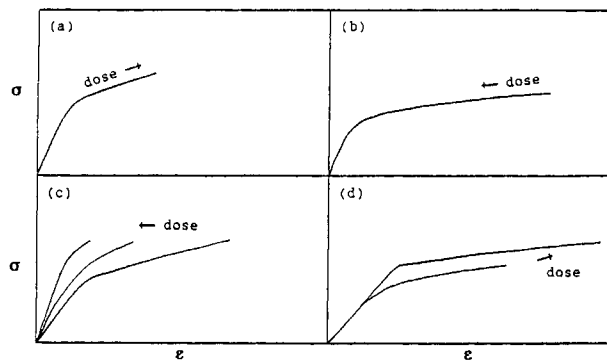


Figure 4 Schematic representation of the effect of EB irradiation on the stress-strain curves of the different polyesters: (a) C6, C6O, (b) C12, (c) C6=, and (d) C12O.

crosslinking dominates in most of the rigid-rod polymers with aliphatic side chains studied. Only the polyester C6 with short alkoxy side chains still has a slight overall tendency for degradation. Crosslinking is favored by longer side chains and by the introduction of hetero atoms that are more easily ionizable, like oxygen. The by far best results are obtained through the introduction of an unsaturation in the side chains.

A fair degree of network formation is a prerequisite if we want to use this method for improving the off-axis properties of oriented structures made from this class of materials. From the data presented, it becomes clear that this can be accomplished by the incorporation of olefinic groups or comparable large side chains. The fact that both the C12O and C6= polyesters show an improvement in mechanical properties upon irradiation qualifies these two materials as most promising for future research on oriented systems. In addition, for the C12 polyester, the gain in off-axis properties may outweigh the slight decrease in tensile properties.

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