

Diacetylene-Containing Polymers VI. Effect of Electron Beam on Mechanical Properties of Poly(octa-3,5-diynylene sebacate) and Poly(hexa-2,4-diynylene sebacate)

Sergei FOMIN, Alfredo MACIEL, and Takeshi OGAWA*

*Instituto de Investigaciones en Materiales, Universidad Nacional Autonoma de México,
Apartado Postal 70-360, Coyoacan, México DF, 04510 México*

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ABSTRACT: The mechanical properties and their dependence on electron beam irradiation were studied for high molecular weight diacetylene-containing thermoplastics: poly(octa-3,5-diynylene sebacate) and poly(hexa-2,4-diynylene sebacate). The tensile strength of the polymers goes through a maximum reaching 330 MPa (with irradiation dose of 0.2 Mrad) for the former and 129 MPa (1 Mrad) for the latter in the case of oriented samples. Further irradiation of the samples leads to decrease in tensile strength, an increase in Young's moduli and decrease in the strain at break. FT-IR spectroscopy of the samples showed that even at 15 Mrad, when tensile strength drops by several times, compared to unirradiated samples, irradiated samples still contain many unreacted diacetylenic groups. Data from thermal mechanical analysis showed that irradiation by 1 Mrad already leads to loss of the thermoplastic properties of material due to polydiacetylene network formation.

KEY WORDS Polydiacetylene / Diacetylene / Polyester / Mechanical Properties /

Oxidative coupling of terminal bis acetylenes has been used since the early 1960s to prepare diacetylene containing polymers.^{1,2} Once monomers are prepared, the synthesis of polymers is quite simple, involving only O₂ and a catalytic amount of CuCl. The monomers are stable and the only byproduct of polymerization is water. Finally, the diacetylene-containing polymers may be cross-linked thermally or by irradiation without volatile side products, thus modifying greatly their properties. A previous investigation of fibers spun from poly(hexamethylene-10,12-docosadiyne-1,22-diamide) prepared by interfacial polycondensation of hexamethylenediamine and 10,12-docosadiyne-1,22-diacid chloride³ showed 100% increase in ultimate tensile strength after exposure to an electron beam of 80 Mrad.

However, the polymers so far prepared by the oxidative coupling reaction generally have molecular weight too low for use as plastics. Recently high molecular weight diacetylene-containing polymers have been prepared successfully by oxidative coupling: Kwoc⁴ reported the synthesis of soluble, high molecular weight poly(aromatic diacetylenes) using mixed solvent *o*-dichlorobenzene (ODCB)-pyridine and a CuCl-*N,N,N',N'*-tetramethylenediamine (TMDA) complex as a catalyst at 80°C. Previously the present authors reported the synthesis of high molecular weight polyamides ($\eta_{inh} > 1 \text{ dl g}^{-1}$) in *N*-methylpyrrolidone⁵ and also of high molecular weight ($\eta_{inh} > 1$) thermoplastic polyesters⁶ in ODCB in the presence of CuCl-TMDA complex.

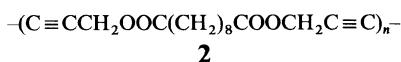
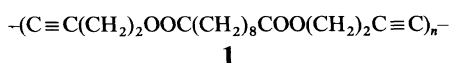
This paper reports the mechanical properties

* To whom correspondence should be addressed.

of high molecular weight diacetylene-containing aliphatic polyesters; poly(octa-3,5-diynylene sebacate) (**1**) and poly(hexa-2,4-diynylene sebacate) (**2**) as well as modification by electron beam irradiation. Polymer **2** was first described by Wegner.⁷ He prepared the polymer starting from 2,4-hexadiyne-1,6-diol and sebacyl chloride and obtained low molecular weight crystalline materials with η_{inh} of 0.1–0.2 dl g⁻¹. Kuhling, *et al.* were the first to prepare **2** by the oxidative coupling of bis(propargyl)-sebacate⁸ in the presence of the CuCl–TMDA complex at 35°C but they failed to obtain high molecular weight polymers. Using the method reported in ref 6 we succeeded in the preparation of **2** with η_{inh} of 1.6 dl g⁻¹.

EXPERIMENTAL

The synthesis of polymer **1** was described earlier.⁶ The polymer has η_{inh} of 1.2 dl g⁻¹ in CHCl₃ at 25°C purified by reprecipitation from CHCl₃ into methanol. Polymer **2** was prepared similarly to polymer **1** in ODCB in the presence of the CuCl–TMDA complex at 75°C and purified similarly to polymer **1**. According to GPC data, M_w were 67000 for polymer **1** and 77000 for polymer **2** with polydispersity index of 3.0 for the both using polystyrene standards.



The samples for mechanical testing were prepared as follows. The purified polymers were heated above their melting point (to 135–140°C for polymer **1** and 100–110°C for polymer **2**) and then pressed into sheets of about 0.1 mm thickness during 30 s. Strips with dimensions of 17 × 5 × 0.1 mm were cut from the polymer sheets and oriented by stretching by 200% at room temperature using an Instron 1125 with a crosshead speed of 5 mm min⁻¹. Irradiation of the oriented samples was carried out with electron beam irradiation in air.

Mechanical testing of the oriented samples was carried out with an Instron 1125 at a crosshead speed of 5 mm min⁻¹ at room temperature, using the Instron series IX automated materials testing system, version 5. Each value given in the mechanical testing data is the mean value taken over five samples. Differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) were performed at a heating rate of 20°C min⁻¹ under a nitrogen flow with a Dupont 2100. Glass transition temperatures (T_g) of the polymers were determined by the intersection method. The samples for TMA were prepared by pressing the polymers into sheets of about 1 mm thickness at a temperature above the melting points. FT-IR spectra of the samples were taken using a Nicolet 510p FT-IR spectrometer. X-Ray diffractometry was performed using a Siemens D-500 diffractometer with Cu- K_α radiation of 1.540 Å. Crystallinity degree of the both oriented and unoriented samples was calculated using program SOCABIM V 3.0 1986, 1991—Copyright Siemens 1991.

RESULTS

Structures and Properties of Original Polymers

As can be seen from the DSC curves (Figure 1) both polymers are thermoplastic, having a mp of 129 and 73°C for polymers **1** and **2** respectively. The DSC curves of the polymers

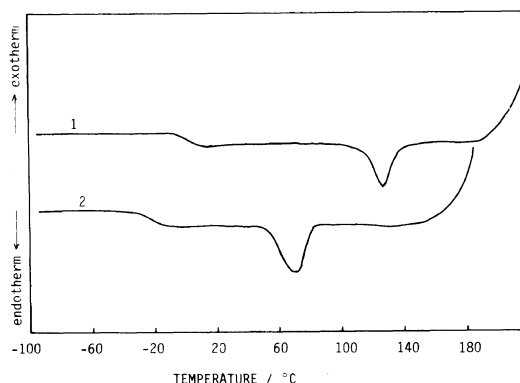


Figure 1. DSC curves of polymer **1** (1) and polymer **2** (2).

taken at low temperature showed a glass transition at 0 and -20°C for polymers **1** and **2** respectively. Thermal cross-linking of the diacetylenic groups starts approximately at 220°C for polymer **1** and at 150°C for **2**, thereby maintaining a region of several tens of degrees for processing from the melt.

At first we tried to prepare fibers from the melt but an explosive decomposition of polymer **1** in the melt took place, probably because of the heat eliminated by the exotherm of the thermal polymerization.

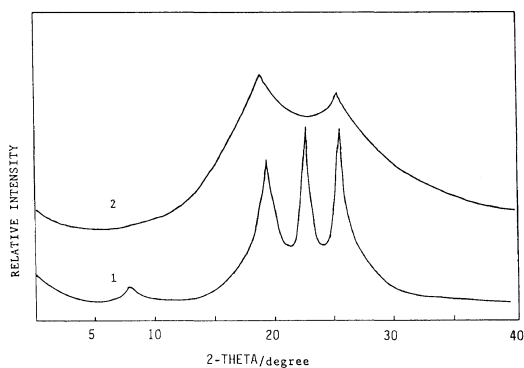


Figure 2. X-Ray diffraction patterns of unoriented polymers **1** (1) and **2** (2).

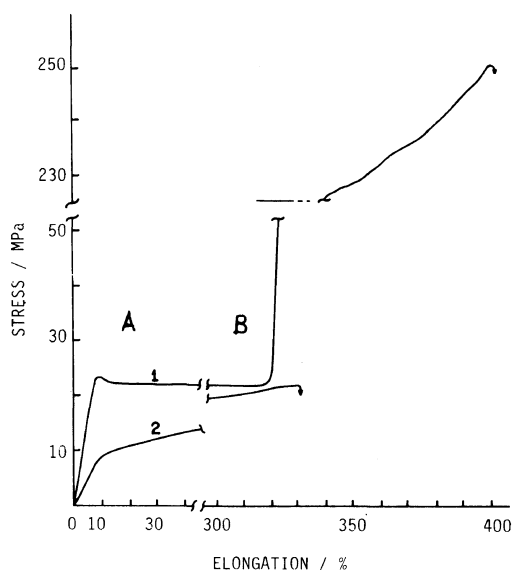


Figure 3. Strain-stress curves of unoriented samples of polymers **1** (1) and **2** (2).

Figure 2 shows X-ray diffraction patterns of unoriented samples of polymers **1** and **2**. As can be seen, polymer **1** is more crystalline than **2**. The calculated degree of crystallinity was 43% for polymer **1** and 25% for polymer **2**.

Strain-stress curves of unoriented samples of polymers **1** and **2** are shown in Figure 3. The shape of the curve of polymer **1** is characteristic of crystalline polymers. At point A the neck formation takes place, and at point B the whole sample is converted to the neck. The limit of flow and Young's moduli of OA part of the stress-strain curve were calculated as 24 and 240 MPa, respectively. The neck material was more crystalline than the unstretched polymer **1** and oriented, as can be seen from X-ray diffraction patterns in two directions,

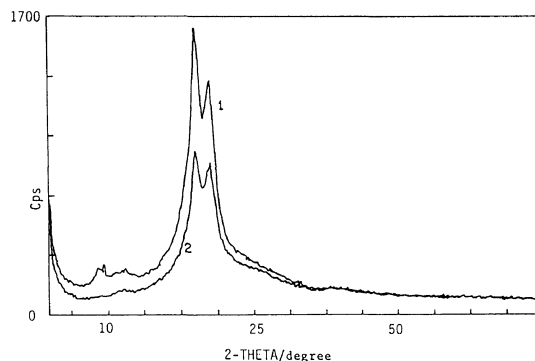


Figure 4. X-Ray diffraction patterns of polymer **1** taken in two directions, parallel (1) and perpendicular (2) to orientation direction.

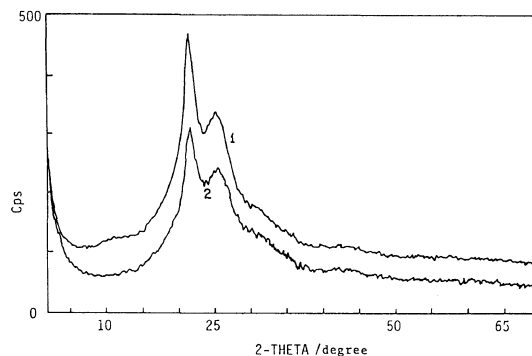


Figure 5. X-Ray diffraction patterns of polymer **2** taken in two directions, parallel (1) and perpendicular (2) to orientation direction.

parallel and perpendicular to the orientation direction (Figure 4). The calculated degree of crystallinity was 64% for the oriented samples. These oriented samples were used to study the effects of electron beam irradiation on the mechanical properties of the polymer. In the case of the stretching of polymer 2, no neck formation took place. X-Ray diffraction patterns taken in two directions, parallel and perpendicular to orientation direction (Figure 5), showed some orientation in this case. An increase in the degree of crystallinity was observed on stretching (Table I). As can be seen from Table I, orientation of the polymers leads to a prominent increase in both the tensile

strength and Young's modulus of the polymers.

Effects of Electron Beam Irradiation

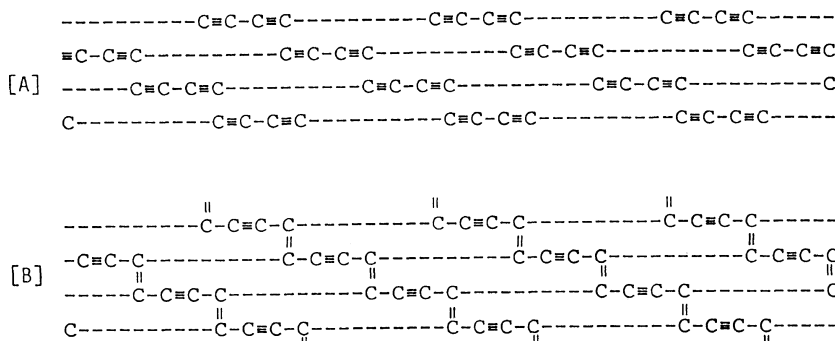
The originally colorless samples turned red on electron beam irradiation and color varied from pale orange to reddish orange depending on the irradiation dose. The topochemical cross-polymerization of diacetylenic groups occurs on irradiation (Scheme 1) to form a polydiacetylene network which strongly affects the mechanical properties of the polymers. The data from the mechanical testing of the irradiated samples are listed in Table I.

As expected, increase in the irradiation dose leads to decrease in the strain at break for the

Table I. Mechanical properties of polymers 1 and 2

Sample	Dose	Strain at break	Tensile strength	Initial Young's Modulus	Degree of crystallinity
	Mrad	%	MPa	MPa	%
Polymer 1	0.	60 (400 ^a)	250 (66 ^a)	1090 (240 ^a)	64 (43 ^a)
	0.05	60	250	1087	64
	0.2	60	330	1093	57
	1	22	220	1240	53
	5	13	180	1380	43
	15	3	48	1630	44
Polymer 2	0	80 (330 ^a)	99 (22 ^a)	203 (78 ^a)	32 (25 ^a)
	0.05	63	96	202	30
	0.2	52	98	205	27
	1	49	129	263	22
	5	12	26	338	20
	15	8	11	350	19

^a Unoriented film.



Scheme 1. Schematic model of polymers containing diacetylene groups in the main chains. [A], before cross-polymerization; [B], after cross-polymerization.

polymers, due to increase in the number of cross-links between the polymer chains, which makes the polymers more rigid. The tensile strength for both polymers goes through a maximum on irradiation, reaching 330 MPa (0.2 Mrad) for polymer 1 and 129 MPa (1 Mrad) for polymer 2. The starting tensile modulus for unirradiated and unoriented polymers was 66 MPa for polymer 1 and 22 MPa for polymer 2.

The reason for the increase in tensile strength on irradiation is that the polymer chains are prevented from sliding by the formation of a polydiacetylene network. Polymer 1 has a tensile strength 3 times higher than polymer 2 and this is reflected in its higher glass transition temperature, melting point and degree of crystallinity. Further irradiation leads to a sharp decrease in tensile strength which dropped to 48 for polymer 1 and 11 MPa for polymer 2.

Figure 6 for polymer 1 and Figure 7 for polymer 2 shows FT-IR spectra of unirradiated and irradiated samples at different doses. The FT-IR spectrum of unirradiated polymer 1 showed 3 absorption peaks corresponding to stretching of the diacetylene groups at 2156, 2202, and 2263 cm^{-1} (peaks A, C, and D in Figure 6 respectively). The spectrum of polymer 1 irradiated with 15 Mrad differs greatly from that of the unirradiated one.

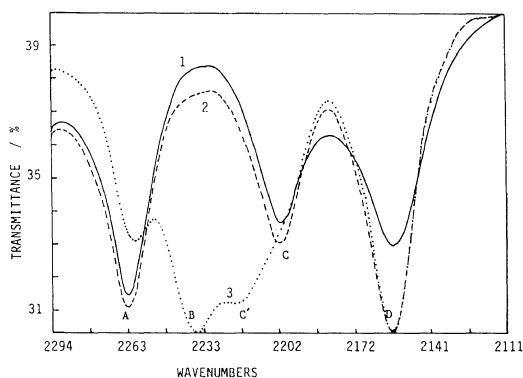


Figure 6. FT-IR spectra of unirradiated samples of polymers 1 (1) and irradiated ones with the doses of 0.2 (2) and 15 (3) Mrad.

Along with diacetylene peaks one can observe the appearance of a new peak (2235 cm^{-1} , peak B in Figure 6), which corresponds to the stretching of $\text{C}\equiv\text{C}$ group of the polydiacetylene chain. This indicates the formation of a rather dense polydiacetylene network. The absorption band of diacetylene groups C (2202 cm^{-1}) shifted to 2218 cm^{-1} in irradiated polymer 1 (peak C' in Figure 6). This may be due to the strain brought about in the polymer 1 during the irradiation. The IR spectrum of polymer 2 shows two diacetylene absorption bands at 2158 and 2263 cm^{-1} (peaks A and C, respectively in Figure 7). On irradiation, a new absorption band appeared at 2220 cm^{-1} corresponding to $\text{C}\equiv\text{C}$ stretches of the polydiacetylene chain (peak B in Figure 7).

Estimation of the conversion of diacetylenic triple bonds to the triple bonds of polydiacetylenic networks (as shown in Scheme 1) was made using FT-IR data for absorption band of diacetylenic group at 2263 cm^{-1} . In the case of polymer 1 the conversions were found to be 20 and 55% at doses of 0.2 and 15 Mrad respectively. In the case of polymer 2 they were 32 and 52% at doses of 1 and 15 Mrad, respectively.

Long-term irradiation of polymers 1 and 2 (5 and 15 Mrad) causes partial amorphization and internal stress in the polymers, because of the high cross-linking density which leads to

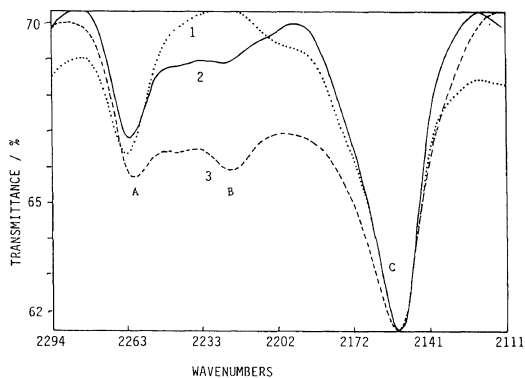


Figure 7. FT-IR spectra of unirradiated samples of polymers 2 (1) and irradiated ones with the doses of 1 (2) and 15 (3) Mrad.

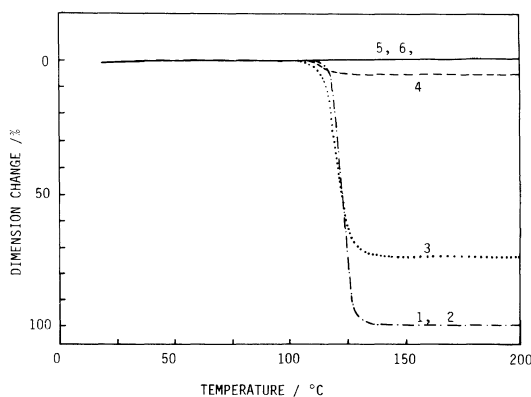


Figure 8. TMA curves of unirradiated polymer **1** (1) and irradiated with 0.05 (2), 0.2 (3), 1 (4), 5 (5), and 15 Mrad (6).

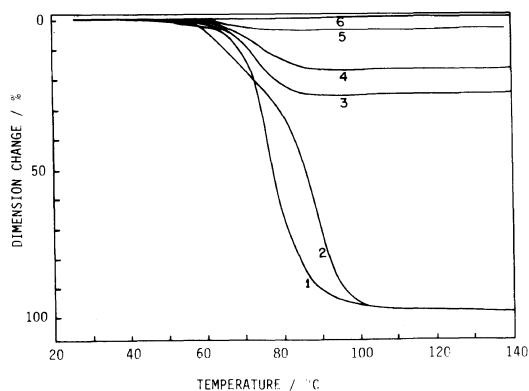


Figure 9. TMA curves of unirradiated polymer **2** (1) and irradiated with 0.05 (2), 0.2 (3), 1 (4), 5 (5), and 15 Mrad (6).

decrease in tensile strength of both polymers.

The Young's modulus of the polymers increased on stretching for both polymers. The Young's modulus also tended to increase on irradiation of the oriented samples, due to increase in material rigidity on irradiation because of cross-linking.

To investigate the effects of irradiation on the softening temperature of the polymers, TMA was performed. Figures 8 and 9 show the TMA curves for polymer **1** and polymer **2**, respectively. The softening temperature of unirradiated polymer **1** (120°C) coincides closely with its melting point (128°C). When irradiated at 0.05 and 0.2 Mrad the softening

point was observed close to the melting point of polymer **1**, but in the latter case, limiting deformation no longer reached 100% which implies a loss of fluidity because of cross-linking. Further irradiation leads to decrease in the limiting deformation which can be barely detected at doses of more than 1 Mrad. Polymer **1** irradiated at doses of 5 and 15 Mrad no longer shows a softening temperature.

Thermomechanical curves for polymer **2** are similar to those of polymer **1**. The unirradiated samples and those irradiated with 0.05 Mrad, still flow when heated to the melting point (limiting deformation 100%). Limiting deformation of the samples irradiated with 0.2 Mrad reached 73% whereas samples irradiated with 5 and 15 Mrad showed no softening temperature.

DISCUSSION

The mechanical properties of high molecular weight diacetylene containing thermoplastic polyesters and their dependence on irradiation with electron beam were studied. The tensile strength of both polymers goes through a maximum on irradiation reaching 330 MPa (0.2 Mrad) for polymer **1** and 129 MPa (1 Mrad) for polymer **2**. The rigidity of the polymers increased continuously on irradiation (strain at break decreased from 300–400% for unirradiated polymers to several percent for the polymers irradiated with 15 Mrad). The increase in rigidity of polymers on irradiation was also reflected in the continuous increase in Young's modulus on irradiation, reaching 1630 MPa for polymer **1** and 350 MPa for polymers **2** after 15 Mrad irradiation.

TMA data show that polymers no longer have a softening point after irradiation with doses in excess of 1 Mrad because of the formation of a polydiacetylene network.

When the maximal tensile strength of the polymer films (330 MPa for polymer **1** and 129 MPa for polymer **2**), are compared with those of industrial polymers such as poly-

ethylene terephthalate (172 MPa, film)⁹ and polyamide 6 (80—90 MPa, film),⁹ and if the ease of monomer preparation, monomer stability and the ease of polymer production together with possibility of modification mechanical, thermal and optical properties by irradiation are taken into account, one can consider diacetylene containing thermoplastic polymers as promising commercial plastics. However, care must be taken in the processing of these polymers, because there is the possibility of explosion when heated at high temperature due to the high exothermic polymerization of diacetylenic groups.

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