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Investigación

Diacetylene-Containing Polymers X. Poly(hexa-2,4-diynylene alkandicarboxylates): Morphology and Properties

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Abstract. In order to study the relationships between the chemical structure, properties and the morphology of diacetylene-containing aliphatic polyesters, a series of diacetylene-containing polyesters having hexa-2,4-diynylene groups were synthesized, and their chemical properties and morphology were investigated. The crystallinity of these polyesters depended on the methylene chain length of the dicarboxylic acids. According to DSC, all of these polymers had an endotherm due to the melting of the crystalline part at around 60 ºC and a large exotherm due to the thermal polymerization in the amorphous state, which occurred above 150 ºC. The polymers were light-sensitive developing yellow to red colors on UV irradiation due to the formation of polydiacetylene network in the polymer films. The polydiacetylene networks formed by UV irradiation degrade on prolonged irradiation in air due to photo-oxidation, except in the case of polyazelate.

Keywords: Diacetylene-containing polymers, polyesters, crosslinking, polydiacetylenes.

Resumen. Con el objeto de estudiar las relaciones entre estructura química, propiedades y morfología de poliésteres alifáticos que contienen grupos diacetilénicos, se sintetizaron una serie de poliésteres que contienen el grupo hexa-2,4-diinileno, y se estudiaron sus propiedades químicas y la morfología de los mismos. La cristalinidad de estos poliésteres dependió de la longitud de la cadena metileno de diácidos carboxílicos. El análisis de DSC demostró que todos los poliésteres tenían señal endotérmica alrededor de 60 ºC correspondiente a la fusión de la parte cristalina, y exotérmica arriba de 150 ºC debido a la polimerización térmica de los grupos diacetilénicos en estado fundido. Los polímeros fueron sensibles a la luz desarrollando color amarillo a rojo por irradiación de luz UV. La irradiación prolongada en aire causó la degradación de los polidiacetilenos formados en los poliésteres, excepto en el caso del azelato.

Palabras claves: Polímeros diacetilénicos, poliésteres, reticulación, polidiacetilenos.

Introduction

The solid state polymerization of diacetylenes is a well-known example of topochemical polymerization in which monomer crystals are converted to the corresponding polymer crystals [1] as shown in Fig. 1. However, because of their extremely high crystallinity their processing into thin films with excellent optical quality is difficult, and this has been the vital disadvantage for their nonlinear optical applications. One of the methods to obtain polydiacetylene thin films is to obtain processable polymers containing diacetylene units, and after processing to thin films, the diacetylene groups are polymerized by irradiation or heating to develop polydiacetylene networks in the films as shown in Fig. 2.

Diacetylene-containing polymers are interesting materials for a variety of potential applications because of their reactive diacetylene (DA) groups, and many different types of DA-containing polymers have been prepared [2, 3]. The DA groups can be cross-polymerized to obtain polydiacetylene (PDA)-containing films which exhibit third order nonlinear optical susceptibility [4]. The reactivity of the DA groups to form a PDA network in the polymer films depends on the crystalline structure of the films, which are determined by the chemical structures of the DA-containing polymers. The reactions with halogens give 1,2,3,4-tetrahalobutadiene-containing polymers [5].

Previously, a series of DA-containing polysebacates were synthesized and their chemical and physical properties were reported [6, 7]. They were semicrystalline polymers and some of them showed an extraordinary mechanical strength; for example, a film of poly(octa-3,5-diynylene sebacate) had a tensile strength of 250 MPa. The polymers developed a reddish color upon irradiation with UV light or electron beams. Therefore, mechanically strong polymer films containing unsaturated bonds are readily obtained. Polymer films having highly unsaturated carbon-carbon linkages are interesting materials for applications in gas separation. Masuda and his coworkers have reported oxygen permeability of poly(1,2-disubstituted acetylenes) which showed excellent results in oxygen permeability [8]. However, the permeability decreases considerably with time, due to oxidation of double bonds by oxygen. Polydiacetylenes, on the other hand are much more resistant to oxidation than polyacetylenes because of the triple bonds in the conjugation. Beckham and coworkers have stu-

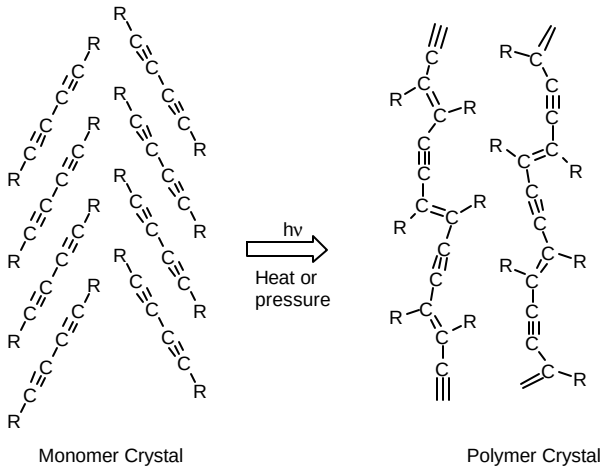

Fig. 1. Polymerization of diacetylenes in the solid state.

died gas separation of a diacetylene-containing polyimide system, observing an increase in the oxygen/nitrogen selectivity [9].

The main objective of this study is to investigate the relationships among morphology, chemical structure and optical properties of the films containing PDA networks developed in the films. The colors of these polymers containing PDA networks vary from pale yellow to deep blue depending on their chemical structure, which cannot be predicted. Therefore, it is worth scanning as many polymers as possible in the hope of finding the best PDA-containing films for nonlinear optical applications. In this work, a series of DA-containing aliphatic polyesters based on the 2,4-hexadiynylene unit were synthesized and their morphology and properties were investigated.

Experimental

Monomer synthesis. The bisacetylenic monomers were synthesized by the reactions of different acid chlorides with propargyl alcohol using triethylamine as an acid acceptor and dichloromethane as a solvent:

$$\mathrm{Cl\text{-}CO(CH_2)_{\mathit{n}}CO\text{-}Cl + 2HC{\equiv}C\text{-}CH_2\text{-}OH}$$
$$\xrightarrow{\mathrm{N\,Et_3,\,CH_2Cl_2}} \mathrm{HC{\equiv}C\text{-}CH_2\text{-}OCO(CH_2)_{\mathit{n}}\text{-}COO\text{-}CH_2\text{-}C{\equiv}CH}$$

where *n* is 2, 3, 4, 6, 7, 8 and 10. The chlorides, 2,3,4,7 and 8 were supplied by Aldrich Chemical and distilled under reduced pressure before use. The chlorides 6 and 10 were prepared by the reaction of the corresponding acids with thionyl chloride. The reaction with propargyl alcohol was carried out in dry dichloromethane using triethylamine as an acid receptor. Prior to use, the dichloromethane was distilled over phosphorus pentoxide or calcium hydride and triethylamine was distilled over barium oxide. After the reaction, the solvent was evaporated and the products were separated from the triethylamine hydrochloride by extracting with acetone. After evaporating acetone, the monomers were distilled under vacuum (2, 3, 6) or recrystallized from hexane (4, 7, 8, 10). It is essential that these bisacetylenic monomers are absolutely pure in order to obtain polyesters with high molecular weights. Table 1 shows characterization data of these bisacetylenic esters.

Polymerization. An oxidative coupling reaction was used for polymerization. To 2 g of the monomer dissolved in 10 mL of distilled *o*-dichlorobenzene, were added 10 drops of freshly distilled N,N,N',N'-tetramethylethylenediamine and 0.085 g copper (I) chloride which had been purified by washing with 20 % sulfuric acid, then by glacial acetic acid, finally by acetone. The system was gently bubbled with oxygen while stirring at 70 °C. The viscosity of the system rapidly increased and in some cases stirring became no longer possible. The contents were poured into HCl-acidified methanol to precipitate the polymer, which was rapidly filtered, washed with methanol and dried in vacuum at room temperature. Immediately after drying the polymers were again dissolved in chloroform, and reprecipitated in methanol. The polymers were light sensitive and they tend to crosslink during storage. Therefore, the polymers were kept in a dichloromethane solution, and recovered by reprecipitation before measurements. The polymers, poly(hexa-2,4-diynylene alcandicarboxylate)s are hereafter abbreviated as 1-*n*, where the numbers of methylene groups of the alcohol (1 from propargyl alcohol) and dicarboxylic acids, respectively.

Instrumentation. DSC and TGA were performed with a Du Pont 2100 thermoanalyzer. The powder X-ray diffractometry was carried out on a Siemens D-500 diffractometer with Cu-K_a radiation of 1.540 Å. The samples were prepared by precipitating the polymer into methanol using somewhat dilute polymer solutions in order to obtain the polymers in the form of fibrous powders. Precipitation from concentrated solutions results in the precipitation of fibrous polymers. Degree of crystallinity was calculated from the difference between the total area and the amorphous area using the software from

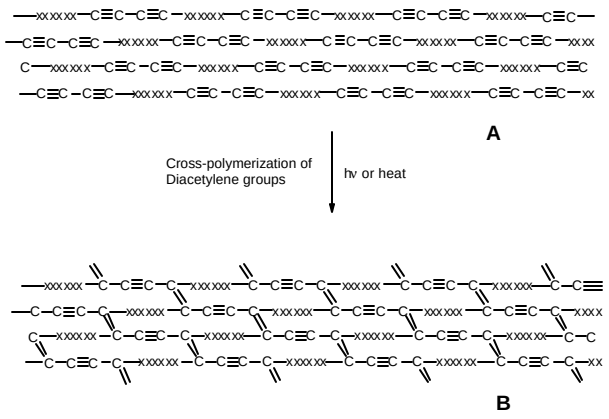

Fig. 2. Schematic diagram of cross-linking in crystallite of photosensitive diacetylene-containing polymers. —xxxxxx—: spacer group such as esters, amides, etc. **A**: Before cross-linking. **B**: After cross-linking by radiation or heat at temperature below melting point.

Table 1. Bisacetylenic monomers (dipropargylalkanedicarboxylates).

Monomer	Melting point ºC	Elemental analysis Found %		Calcd.%	
		C	H	C	H
1-2 (succinate)	33.5	61.25	5.28	61.86	5.15
1-3 (glutarate)	liquid	63-10	5.32	63.46	5.77
1-4 (adipate)	30	64.78	6.28	64.86	6.31
1-6 (suberate)	liquid	66.97	7.02	67.20	7.20
1-7 (azelate)	liquid	67.69	7.53	68.18	7.57
1-8 (sebacate)	27	69.25	7.55	69.06	7.91
1-10 (decanedicarboxylate)	38	70.44	8.67	70.59	8.50

Table 2. Crystallinity of polyesters.

Polymer	Crystalline part %	Amorphous part %
1-2	54.2	45.8
1-3	37.4	62.6
1-4	36.8	63.2
1-6	39.2	60.8
1-7	41.2	58.8
1-7 Partially crosslinked	34.8	63.2
1-7 Totally crosslinked	2.8	97.2
1-8	43.5	56.5
1-10	48.1	51.9

Siemens DIFFRAC AT, Version 3.2. The molecular weights of the polymers were determined in chloroform solution by GPC using a Waters 150C with polystyrene standard.

UV/Visible absorption spectra of the films spin-coated from dichloroethane solution were taken using a UNICAM model UV300 spectrophotometer. The films were irradiated with a medium pressure mercury lamp supplied by Ace Glass.

Results and discussion

The molecular weights of these polymers determined by GPC are in the range of 15,000-20,000 with a polydispersity around 1.5. All of these polymers were light- and heat-sensitive. They develop colors on standing at room temperature even in the dark. X-ray diffraction patterns of these polymers are shown in Fig. 3 and their crystallinity is shown in Table 2. The crystallinity of poly 1-2 was found to be the highest among these polymers, and the low crystallinity of poly 1-3 is due to the odd number of methylene group. In general the crystallinity increased with increase in methylene chain length. However, crystallinity of these DA-containing polyesters decreases drastically with crosslinking [7]. An intense red carmine Poly 1-7 cross-polymerized through its diacetylenic groups showed a crystallinity of only 2.8 % indicating that the polymer became almost completely amorphous by cross-linking (Table 2 and Fig. 4). Since it is impossible to avoid the cross-polymerization of diacetylene groups by X-ray during the measurement which takes about one hour, the crystallinity of original polymers before the measurement should be higher than the values shown in Table 2.

The typical DSC curve of some of these polyesters is shown in Fig. 5. Table 3 summarizes the thermal behavior of these polyesters, which have endothermic peaks due to the melting of the crystalline region (crystallites) starting around 60 ºC. This melting temperature seems to be characteristic to the hexa-2,4-diynylene esters, and seems independent of the methylene chain length of the diacids. It seems that the methylene chain length influence the crystallite form. In the cases of poly(octa-3,5-diynylene alkandicarboxylates) the melting temperature depends on the number of methylene chains of the diacids. The melting point of poly(octa-3,5-diynylene sebacate) is around 130 ºC [7], while that of poly(octa-3,5-diynylene azelate) is 70 ºC [10]. The heat required for melting the crystallites differed depending on the acid methylene length. The heat required for melting the crystallites in general corresponds to the amount of the crystallites in the polymer. Polymer 1-2 has highest crystallinity and thus it has the highest heat of melting. However, Polymers 1-6 and 1-7 have very small heat for melting although its crystallinity is relatively high. Although the reason for this is not clear, it may be said that Polymer 1-7 forms rather lose crystals probably due to its odd number of methylene group. These observations indicate that in the case of poly(hexa-2,4-diynylene alkandicarboxylate)s the hexa-2,4-diynylene group is the dominating group for crystallization, while in the case of poly(octa-3,5-diyny-

Table 3. Thermal behaviors of polyesters by DSC.

Polyesters	Melting			Polymerization		
	Starting ºC	Maximum ºC	*DH* cal / g	Starting ºC	Maximum ºC	*DH* cal / g
1-2	62	89	26.8	135	182	164
1-3	60	75	11.5	110	157	104
1-4	55	73	13.2	120	162	129
1-6	55	70	6.0	145	190	145
1-7	56	74	2.7	152	198	153
1-8	55	76	9.3	150	205	141
1-10	65	75	16.4	150	200	141

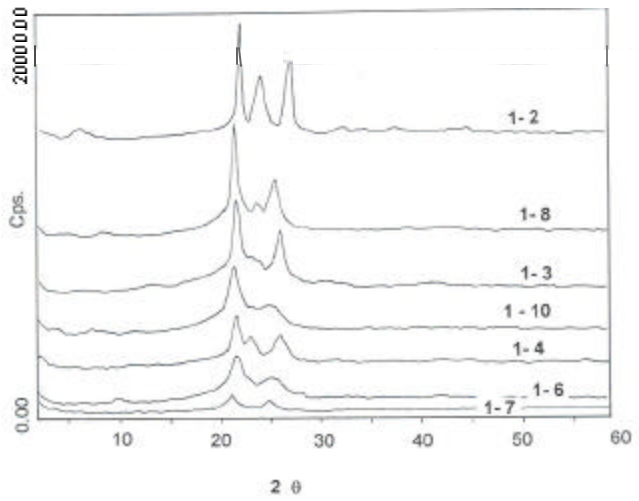

Fig. 3. X-ray diffraction patterns of the poly(hexa-2,4-diynylene dialkanoate)s taken for the powder samples.
1-2: succinate, 1-3: glutarate, 1-4: Adipate, 1-6: suberate, 1-7: azelate, 1-8: sebacate, 1-10: decanedicarboxylate.

lene alkandicarboxylate)s the methylene chains are the main driving force of crystallization. The peaks above 150 ºC are due to the thermal cross-polymerization of DA groups in the molten state, and they do not contain the exotherm due to thermal decomposition, which takes place at temperature above 300 ºC for these polymers.

The absorption spectra in the visible region of spin-coated and irradiated films are shown in Fig. 6. Unirradiated films do not have absorption in the visible region. The transparency of the thin films was acceptable for all the polymers, but the films were those of semi-crystalline polymers, being opaque for thick films. The visible spectra of irradiated polymers vary considerably depending on the polymer structures. The polymer 1-7 was the only case where absorption intensity increased slowly with the irradiation dose and the others rapidly reached the maximum absorption peak after 20 minutes of irradiation, then the absorption peak height decreased with further irradiation, probably because the conjugation systems are broken by photochemical oxidation of the films. Such photodegradation has been also observed for the Langmuir-Blodgett membranes of aromatic PDAs [11]. The photodegradation is due to the oxidation of the conjugated system by the singlet oxygen formed by the energy given to oxygen by the photoexcited conjugated system. The irradiation in the absence of oxygen does not cause such photodegradation [11]. The spectra of polymer 1-7 demonstrated the highest optical density, meanwhile the others showed less than one third of polymer 1-7 at 500 nm region. Its spectra shape and λ_{max} around 500 nm is typical absorption spectra of aliphatic PDAs. It seems that polymer 1-7 has the best crystal packing of diacetylene groups for its topochemical cross-polymerization, although its crystallinity is lower than that of 1-2, 1-8 and 1-10, while the heat of melting of the crystalline part is very small. With respect to the shape of spectra, Polymers 1-2, 1-3 and 1-4 did not show spectra with pronounced peak around 500 nm. This suggests that the cross-linking length is small and the PDAs mainly consists of short oligomeric chains. It seems there is no clear relationship between the favorable crystal packing of diacetylene groups and the crystallinity of polymer chains as a whole. The crystallization of these polyesters originates from different parts of the polymer chain: (a) whole polymer chain, (b) methylene chains of the diacids, and (c) rigid diacetylene moiety. It is difficult to say which of these factors apply to each polymer, but it can be said that in the cases of polymers 1-8 and 1-10, the long methylene chains are the main crystallization force. In the case of 1-7, the crystallization by the methylene chain is difficult due to its odd number, and the rigid diacetylene groups can be the nucleus of crystallization (c).

In order to see if all of the diacetylene groups of these polymers participate in topochemical cross-polymerization, IR spectra were taken for the irradiated films, which had been spin-coated on a KBr disk. However, because of the weak bands of DA bond at the region of 2100-2200 cm^{-1} quantitative determination was difficult, and some DA groups appea-

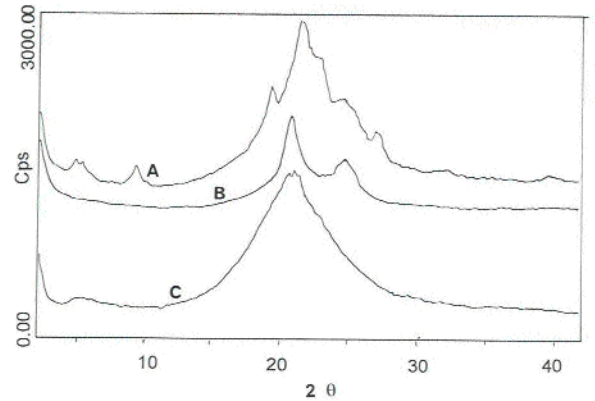

Fig. 4. X-ray diffraction patterns of polyester 1-7. **A**: Before irradiation with UV lamp. **B**: Partially crosslinked by the topochemical crosspolymerization. **C**: Totally crosslinked, a deep red polymer after extracting the soluble part.

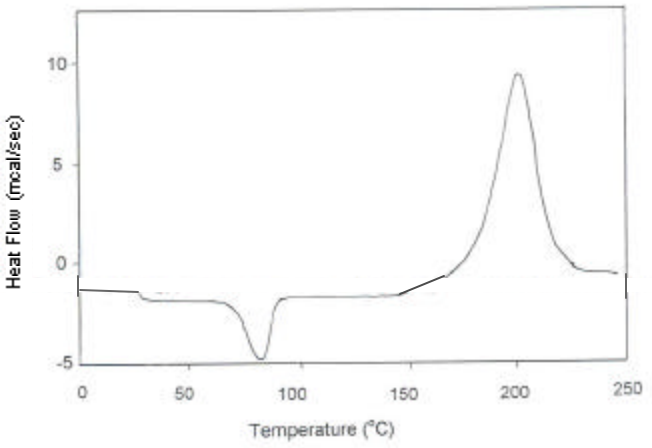

Fig. 5. A typical DSC curve of the polyester (1-10).

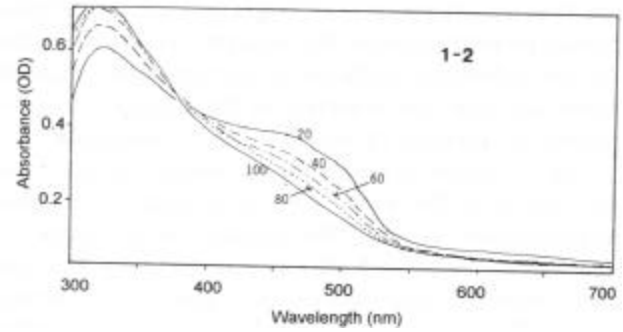

Fig. 6a. Poly(hexa-2,4-diynylene succinate). Thickness: 2.8 μm. Irradiation time (min.) 1: 20, 2: 40, 3: 60, 4: 80, 5: 100.

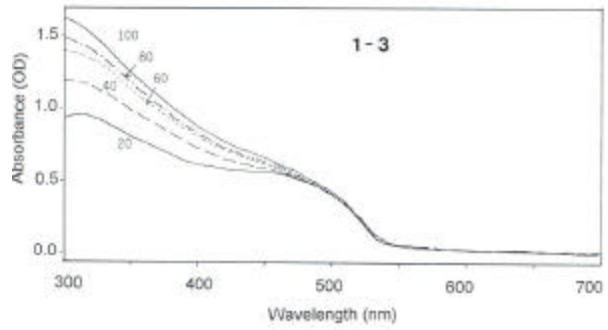

Fig. 6b. Poly(hexa-2,4-diynylene glutarate) Thickness: 3.6 μm. Irradiation time (min.) 1:20, 2:40, 3:60, 4:80, 5:100.

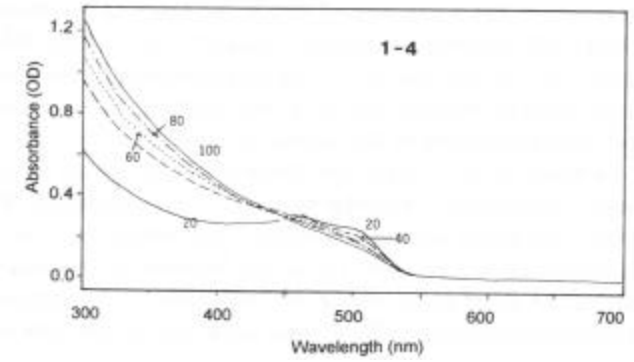

Fig. 6c. Poly(hexa-2,4-diynylene adipate) Thickness: 2.2 μm. Irradiation time (min.) 1:20, 2:40, 3:60, 4:80, 5:100.

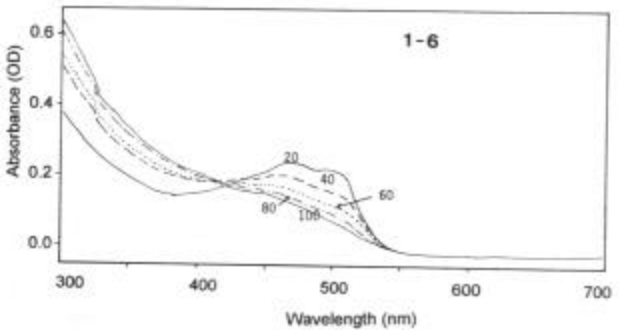

Fig. 6d. Poly(hexa-2,4-diynylene suberate) Thickness: 2.1 μm. Irradiation time (min.) 1:20, 2:40, 3:60, 4:80, 5:100.

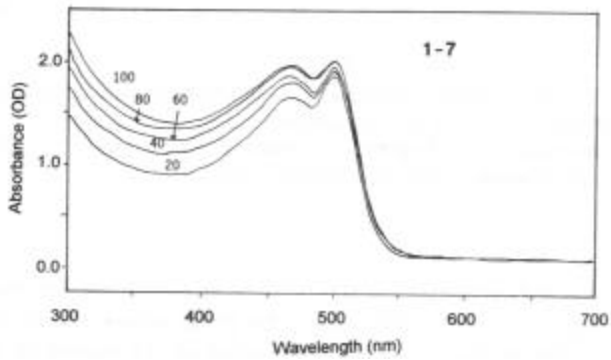

Fig. 6e. Poly(hexa-2,4-diynylene sebacate) Thickness: 2.1 μm. Irradiation time (min.) 1:20, 2:40, 3:60, 4:80, 5:100.

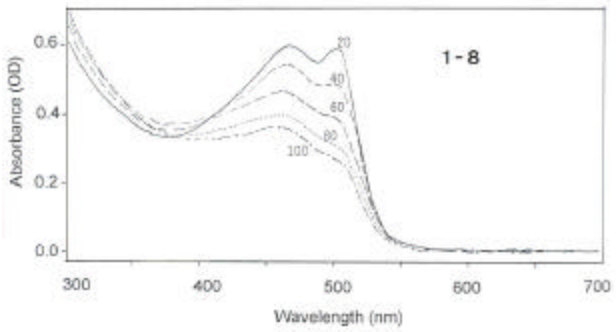

Fig. 6f. Poly(hexa-2,4-diynylene azelate) Thickness : 6.1 μm. Irradiation time (min.) 1: 20, 2:40, 3:60, 4: 80, 5:100.

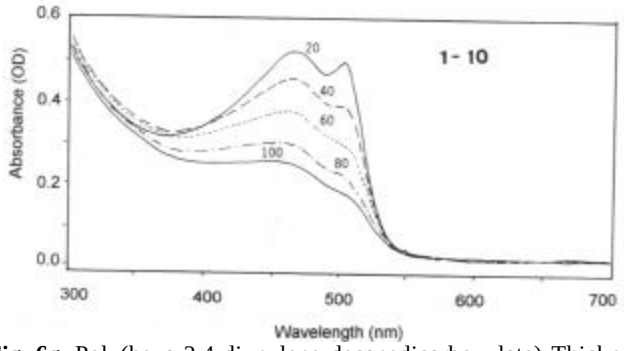

Fig. 6g. Poly(hexa-2,4-diynylene decanedicarboxylate) Thickness: 5.2 μm. Irradiation time (min.) 1: 20, 2:40, 3:60, 4:80, 5:100.

Fig. 6. Visible absorption spectra of spin-coated films of poly(hexa-2,4-diynylene dicarboxylate)s. The numbers on the spectra correspond to the irradiation time in minutes.

red to remain unreacted. In order to see what percentage of the DA groups is in the crystalline part which participate in topochemical polymerization, the cast films were irradiated by UV light between 2 quartz panes, and the irradiated films were analyzed by DSC. The DA groups in the crystalline region will polymerize by irradiation, but those in the amorphous region do not. However, the exotherm peaks starting at 150 °C did not differ significantly before and after irradiation and did not provide the information on the remaining DA groups (mainly in the amorphous parts of the polymers). The thermal polymerization of these DA groups in the molten state probably includes various reactions not only cross-polymerization but also reactions between the triple bonds and double bonds formed between DA groups. Therefore, the polymerization in the molten state is not a favorable method for obtaining ordered structured polymeric materials. It is important to obtain such polymers with high contents of the nanocrystallites in which the DA groups undergo topochemical polymerization by irradiation at room temperature. The colors and their intensities of such PDA-containing polymers differ considerably among individual polymers and it is possible to find the most ideal DA-containing polymers through experimentation.

As far as the concentration of PDA in the polymer is concerned, in the case of a common Langmuir-Blodgett membrane consisting of *n*-$C_{12}H_{25}$-C≡C-C≡C-$(CH_2)_8$-COOH for example [12], the DA content is 4C / (28C + 42H + 2O) = 48 / 412 = 0.128. In the case of polymer 1-7, the DA content is 4C / (15C + 18H + 4O) = 48 / 262 = 0.183. Therefore, the DA contents of DA-containing polymers are usually higher than that of Langmuir-Blodgett membranes. The most important advantage of such DA-containing polymers, is their easy processability, as they can be made into thin films of desired thickness by means of spin coating or casting. DA-containing polymers which give high conversion of topochemical cross-polymerization of their DA groups should be sought. So far aliphatic polyesters containing hexa 2,4-diynylene unit were investigated in this work, and those containing octa-3,5-diynylene were previously studied [6]. These polyesters developed yellow, orange and red colors on exposure to radiation or heat. In the cases of polyesters containing deca-4,6-diynylene and dodeca-5,7-diynylene groups some polymers developed blue and purple coloring [10]. It is interesting to observe how the chemical structure of these DA-containing aliphatic polyesters influence significantly but without any rule the PDA formation which solely depends on the crystal packing of the crystallites. Their gas separation properties of these PDA-containing polyesters are of interest, and they are being studied and will be reported in future.

Conclusion

A series of 7 diacetylene-containing polyesters were synthesized from propargyl alcohol and 7 aliphatic diacids with different numbers of methylene groups. The melting temperatures of these polymers (crystalline region) were more or less the same being in the range of 55-60 ºC indicating that the melting point depends on the diacetylene groups, and not on the acid methylene chains. Among these polyesters, the azelate polymer 1-7 appeared to be most interesting from the point of view of third order nonlinear optical property because of its intense coloring and absorption intensity. The reason why polymer 1-7 is more resistant to the photodegradation than others is not known. For photonic applications, an important issue is how to increase efficiency of cross-polymerization of DA groups in the polymer films, as it seems that not all DA groups in the polymer participate in the topochemical polymerization. Relationships among chemical structure, crystallization and cross-polymerization of DA groups, are very much complex, and it is difficult to predict before synthesis the morphology and chemical properties of this type of polymers containing diacetylene groups in the main chains. There are still interesting problems to be studied in future for these polymers not only their properties for applications but also their novel processing to highly nanocrystalline films.

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