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Diacetylene containing polymers

I. Poly(m,m′-butadiynylene dibenzylterephthalate)

Josefina Pérez[1], Guillermina Burillo[1], Martha Roa[2], Carmen Vázquez[2], and Takeshi Ogawa[2,]*

[1]Instituto de Ciencias Nucleares, and [2]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510-México, Mexico

ABSTRACT

A polyester containing diacetylenic units in main chain was prepared by the polycondensation of m, m'-butadiynylene dibenzyl alcohol with terephthaloyl chloride. The polymer was crystalline, and bearly soluble in hot dimethylformamide or dimethylsulfoxide, but insoluble in most organic solvents. It melts at about 200 ° C. Irradiation of UV light at 75 ° C gave a reddish brown resin. Heating at temperatures above its melting point gave a shinning black hard solid.

INTRODUCTION

The topochemical polymerization of diacetylenes has been studied extensively since Wegner [1] first reported for some diacetylenes in 1969. More recently the nonlinear optical properties of polydiacetylenes attracted much attention [2], and many studies have been reported [3]. The majority of polydiacetylenes however, do not give large crystals, and their processability is not satisfactory. The Langmuir-Blodgett technique is considered as a useful method to obtain crystalline polydiacetylene films [4], although the processing is not so easy. One simple method to obtain polydiacetylene films or sheets is to prepare processable polymers containing diacetylenes, and to polymerize them in the polymer, although the crystallinity of polydiacetylene may be sacrificed. Such systems include the polymers containing diacetylenic groups in side chain [5], and in main chains. The latter case has been reported by various workers. Baldamova, et al. [6] have reported in 1967 the polymerization of aromatic bisacetylenes such as diethynyldialkoxybenzenes by oxidative coupling reaction in the presence of pyridine and cuprous salts. Hey, et al. [7] have prepared various diyne containing polymers. Wegner [8] has also reported diacetylene containing polyester and polyurethane, which developed deep red color on exposure to UV light. Lando and coworkers [9] have studied some poly(alkadiyne) systems. More recently, a polyimide derived from p, p′ -diaminodiphenylbutadiyne and pyromellitic acid has appeared in a patent [10], and the polymer is said to have a very high mechanical strength.

The present authors are synthesizing various unsymmetrical diacetylenes, and obtained m-ethynylbenzyl alcohol as an intermediate. Therefore it was converted to a diacetylenic dibenzyl alcohol, and reacted with terephthaloyl chloride to obtain poly(m, m′-butadiynylenedibenzylterephthalate). The synthesis and thermal behaviors of the polymer are reported in this paper.

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*To whom offprint requests should be sent

EXPERIMENTAL

(1) m-Ethynylbenzyl alcohol.

100 g of freshly distilled m-bromobenzaldehyde (Aldrich Chemical, Co.) and 55 g of 2-methyl-3-butyn-2-ol (Farchan Laboratories) were dissolved in 300 ml of dry triethylamine and 300 ml of dry pyridine in a 1 l, 3-necked flask fitted with a condenser, a nitrogen inlet and a stirrer. While passing dry, oxygen-free nitrogen in the system, 1 g of copper(I) iodide and 1 g of triphenylphosphine were added, and the system was heated to 50 ° C, and 1 g of bis(triphenylphosphine) palladium (II) dichloride was added. The mixture was gently refluxed for 24 hrs. under dry, oxygen-free nitrogen. After the reaction the crystals of triethylamine hydrobromide were filtered, washed with triethylamine. The mother liquors were put togther, and evaporated under a reduced pressure. The residue was poured into 2000 ml of dilute hydrochloric acid, and extracted with ether. Ether was evaporated, and the crude m-3-methyl-3-hydroxy-1-butynyl benzaldehyde thus obtained was reduced to the benzyl alcohol with an excess sodium borohydride in ethanol, and it was then dissolved in 500 ml of n-propanol containing 50 g of sodium hydroxide. After refluxing for 48 hrs, n-propanol was evaporated under a reduced pressure, and the residue was distilled in vacuum. A transparent liquid with bp. 90 ° C/0.1 mmHg was obtained. The overall yield with respect to bromobenzaldehyde was 53 %. Elemental analysis: Calcd. for C_9H_8 O, C:81.82 %, H:6.06 %; Found: C:81.52 %,H:6.2 %.

(2) m, m'-Butadiynylene dibenzyl alcohol.

26.3 g Of the ethynylbenzyl alcohol and 12 g of ammonium chloride were dissolved in 100 ml of methanol, and 4 g of copper (I) chloride were added. Oxygen was then passed for 40 hrs with stirring at room temperature. Small amount of water are added to rinse the solid deposited on the upper part of the reaction flask. The system became yellowish green. 150 ml of 2N hydrochloric acid were added to the system, and the product was extracted with ether. The ether extract was washed with dilute aqueous ammonium hydroxide solution. On evaporation of ether a pale yellow solid was obtained, which was then washed with hexane to remove the unreacted benzyl alcohol, and dried in vacuun. The yield was 57 %. Recrystallization from methanol gave colorless crystals melting at 152-153 ° C. Elemental analysis: Calcd. for $C_{18}H_{14}O_2$:C:82.44 %, H:5.3 %; Found: C:81.95 %, H:5.5 %.

The oxidative coupling reaction was also carried out using pyrydine as a solvent. The yield was low being only less than 20 % and required a large amount of copper (I) chloride.

(3) Polymerization.

10 g Of the dibenzyl alcohol and 7.75 g of terephthaloyl chloride were dissolved in 60 ml of dry dichloromethane, and dry triethylamine was added dropwise avoiding excess exotherm. The viscosity started increase, and then a white powder started to precipitate. After 3 hrs of stirring the polymerization mixture was poured into 200 ml of methanol and the precipitated polymer was filtered, washed well with methanol and dried in vacuum. 14.9 g of a white powder was obtained (99.6 % yield). Elemental analysis: Calcd: for $C_{26}H_{16}O_4$: C:79.59 %, H:4.08 %, Found: C:79.37 %, H:4.2 %.

The polymer was dissolved in boiling dimethylformamide, and reprecipitated on cooling to room temperature, filtered, washed with methanol and dried, before submitting to the measurements.

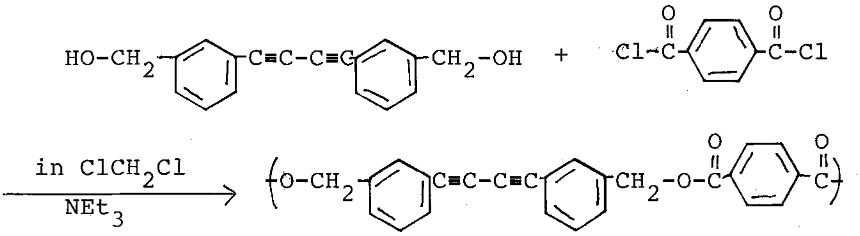
(4) Measurements.

A polarized optical microscope, Olympus BHC fitted with a Leitz heating device, was used for microscope observations. The X-ray difractometry was performed using a Siemen's D-500 diffractometry with CuK α1 radiation of 1.5406A. A DuPont differential scanning calorimeter Model 910 was used for the thermal analysis.

The molecular weight of the polymer could not be determined because it was only slightly soluble in boiling dimethylformamide or dimethylsulfoxide. The polymer became black when it was added into concentrated sulforic acid, and did not disolve.

RESULTS AND DISCUSSION

H-1 NMR spectra of m-ethynylbenzyl alcohol and m, m'-butadiynylene dibenzyl alcohol are shown in Figs. 1 and 2, respectively, IR spectra of the diyne and the polymerization product are shown in Fig. 3. From these spectra and the results of elemental analysis, it is obvious that the following polycondensation took place:



An X-ray difraction pattern of the polymer is shown in Fig. 4. The patterns of the polymer before and after the purification by recrystallization from hot dimethylformamide, were identical. Fine crystals were observed under the microscope, which disappeared on melting at about 200 ° C. The molten polymer crystallized on cooling. It melted again on heating to 213 ° C, and crystallized again on cooling to 180 ° C. Repeating the heating-cooling cycle increased the color of polymer; from pale yellow to orange. Finally when heated to 244 ° C it lost fluidity and became a red solid.

Fig. 5 shows probable Tg of the amorphous part of the polymer. Fig. 6 shows DSC curves of the polymer and that preheated at 250 ° C for 1 hr. The polymer melted at about 200 ° C indicating that no crosslinking took place by heating at 195 ° C (A).

An exothermic polymerization started after melting at about 210 ° C. The heating was stopped at 225 ° C, and the sample was left to stand to cool. The same sample was then heated again (B), and the polymer was no longer fusible, but it kept polymerizing at temperature above 200 ° C. The repetition of this process showed a similar behavior (C). The endotherm peaks observed for B and C at around 130 ° C are attributed to the evaporation of small amounts of volatile thermal decomposition products formed by heating to 225 ° C. The polymer became shinning black after the 3 rd run. The curve D is of the polymer preheated at 250 ° C for 1 hr in a vacuum-sealed Pyrex tube. The polymer is jet black. The small endotherms at about 75 and 130 ° C are probably due to the evaporation of volatiles formed during heating. It seems that the polymerization of diacetylenic groups has been completed by heating at 250 ° C for 1 hr. In order to see the magnitude of thermal decomposition of the polymer, thermal gravimetric analysis (TGA) was carried out and the

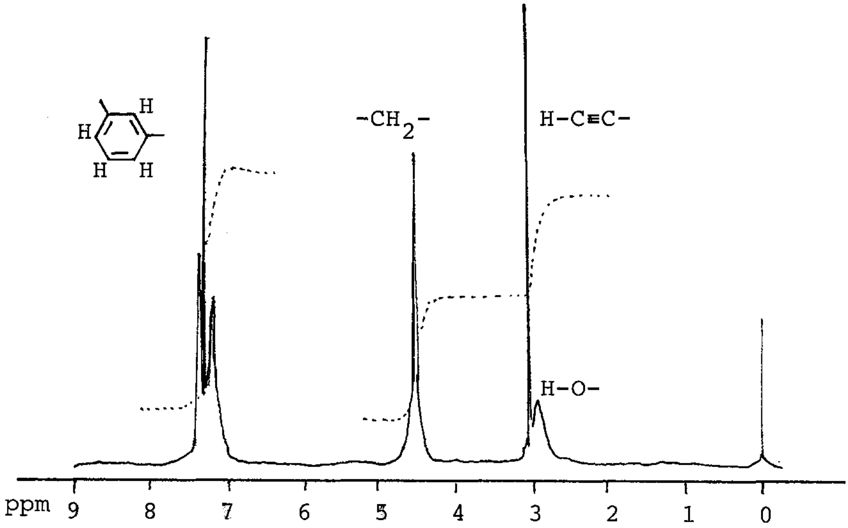


Fig. 1. H-1 NMR spectra of m-ethynylbenzyl alcohol. (CDCl$_3$)

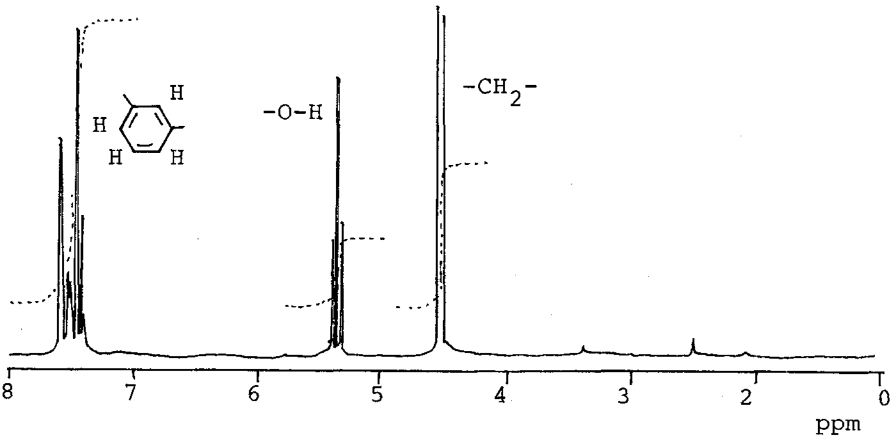


Fig. 2. H-1 NMR spectra of m, m'-butadiynylene dibenzyl alcohol (dMSO).

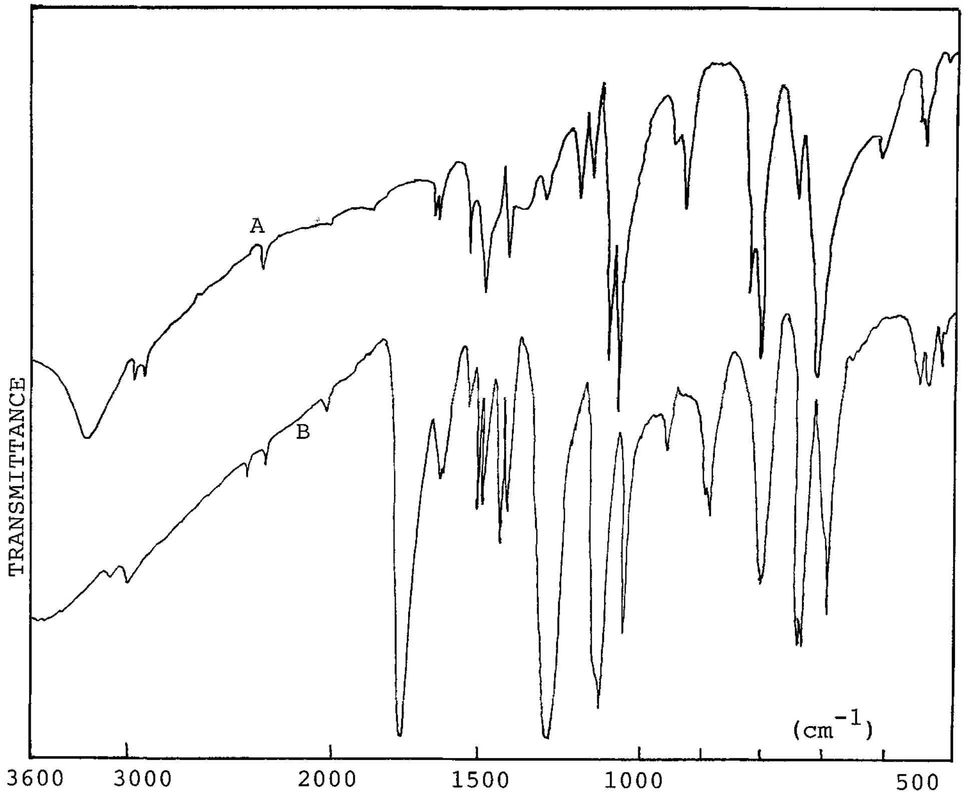


Fig. 3. IR spectra of m, m'-butadiynylene dibensyl alcohol (A) and the polymerization product (B).

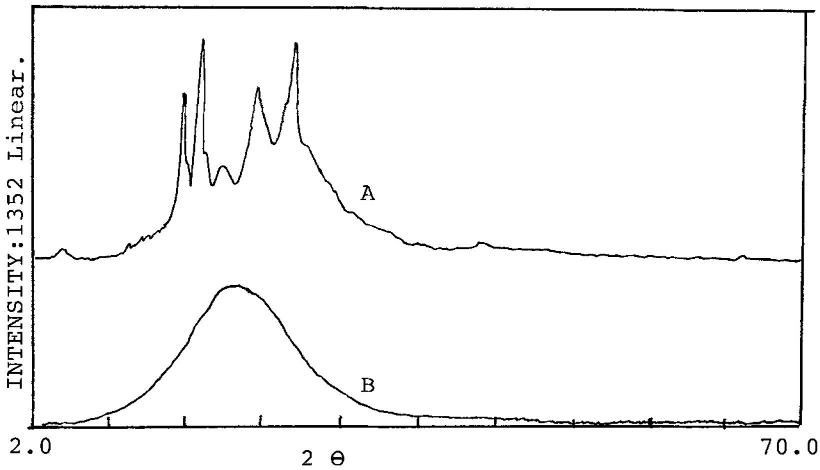


Fig. 4. X-Ray difraction patterns of poly(m, m'-butadiynylene dibenzyl teraphthalate) (A), and of the polymer treated at 250 ° C for 1 hr. (B).

result is shown in Fig. 7. About 1-2 % of weight loss was observed at temperatures above 200 ° C, but no significant decomposition was observed at below 400 ° C. This result indicates that the large exotherm observed at above 200 ° C isdue to the thermal polymerization of diacetylenic groups.

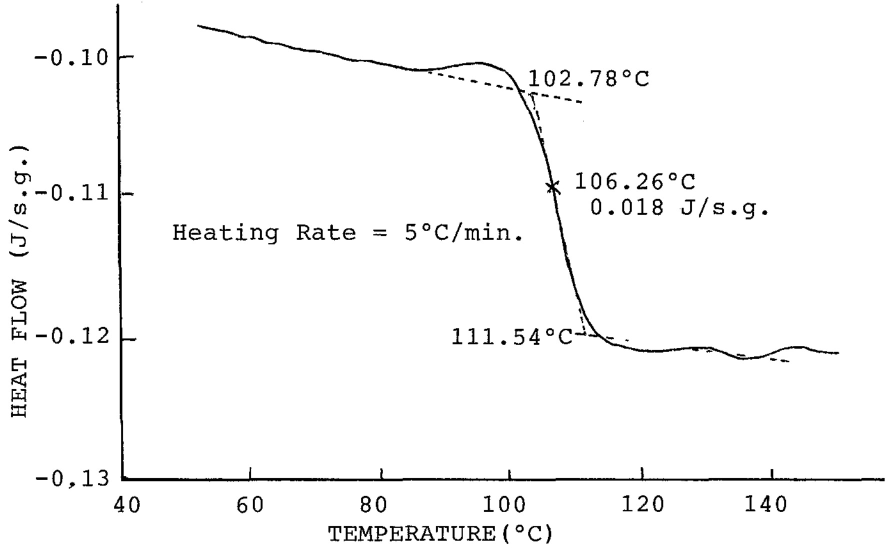


Fig. 5. A DSC curve for poly(m, m' -butadiynylene dibenzylterephthalate).

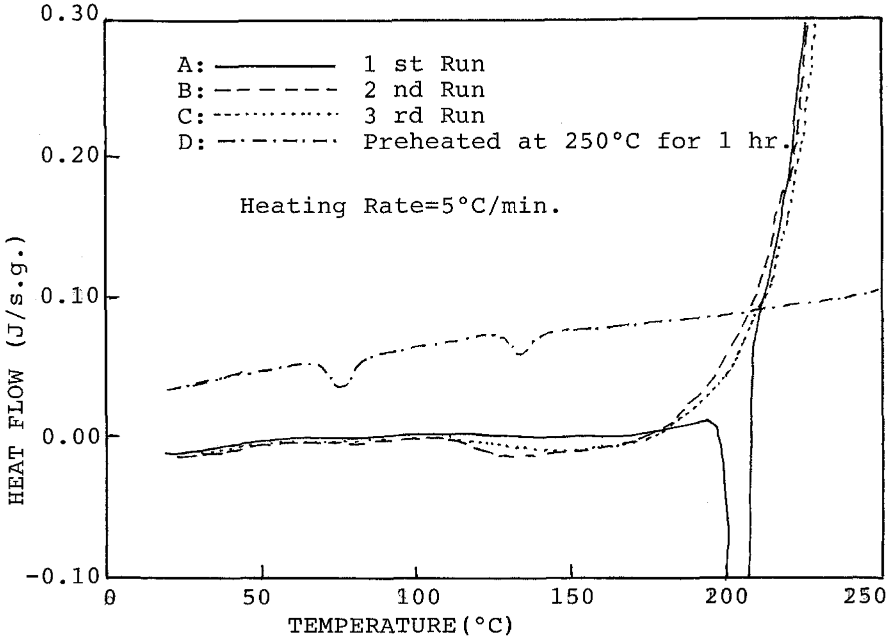


Fig. 6. DSC curves of poly(m, m'-butadiynylenedibenzil terephtalate).

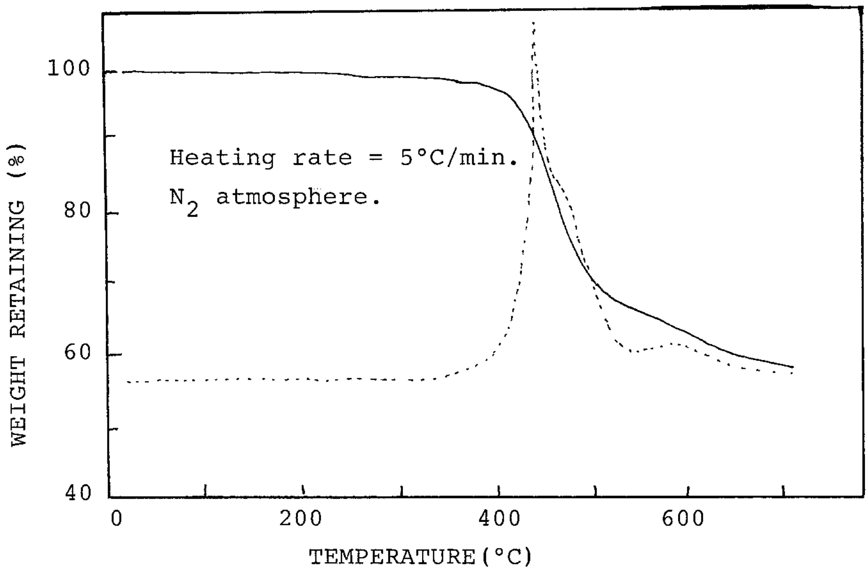


Fig. 7. TGA Curve of poly(m, m'-butadiynylenedibenzyl terephthalate).

The polymer was sandwitched between 2 quartz plates and heated to melt. It was then irradiated at 75 ° C with medium pressure mercury lamp for 5 hrs. Sandwitched film became deep red brown. The X-ray diffraction pattern of this irradiated polymer was almost same as that shown in Fig. 4 (A), being still crystalline.

From the results described above, it can be concluded that the diacetylenic groups in poly(m, m' -butadiynyldibenzylterephthalate) do not polymerize thermally below its melting point, but they rapidly polymerize in the molten state to give a black amorphous material.

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