

## Diacetylene-Containing Polymers IX.<sup>†</sup> Halogenation of Some Diacetylene-Containing Polyesters

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**ABSTRACT:** The chlorination and bromination of some diacetylene-containing polyesters in the solid state and solution were investigated. The solid state bromination of the crystalline poly(octa-3,5-diynylsebacate) took place smoothly at room temperature giving a new polyester containing 1,2,3,4-tetrabromobutadiene units, while chlorination caused the topochemical crosspolymerization of the diacetylene groups instead of addition of chlorine atoms. The solid state bromination of the amorphous polyester was very slow, but both chlorination and bromination in chloroform solutions readily took place giving tetrahalogenated butadiene-containing, totally amorphous polymers. Degradation during halogenation was minimum. The mechanisms of these halogen addition reactions are discussed based on the results of spectroscopic studies.

**KEY WORDS** Diacetylene-Containing Polymers / Polyester / Bromination / Chlorination /

Recently, there have been reported various diacetylene (DA)-containing polymers which can be processed into thin films, and the crosspolymerization of their diacetylene groups has been studied in order to obtain new materials with possible applications in nonlinear optics and optoelectronics.<sup>1</sup> The films containing light-sensitive diacetylene groups showed third order nonlinear susceptibility of  $10^{-10}$ – $10^{-9}$  esu<sup>2</sup> although their optical quality remains to be improved. Highly transparent, polydiacetylene-containing films with  $\chi^{(3)}$  of the order of  $10^{-10}$  esu can be obtained by the amorphous state crosspolymerization of some diacetylene-containing polymers.<sup>3</sup> Apart from their potential applications in nonlinear optics, some diacetylene-containing polyesters provide interesting materials with extremely high tensile strength, *i.e.*, over 300 MPa.<sup>4</sup> However, thermal melt processing of these diacetylene-containing polymers is accompanied with risk of possible explosion when overheated, due to the extremely high exothermic nature of the crosspolymerization of diacetylene groups. An alternative utilization of diacetylene-containing polymers is the synthesis of novel polymers by chemical modifications of the diacetylene groups. It is known that diacetylenes suffer halogenation, reactions with primary amines to form pyrrol ring,<sup>5</sup> and with alkali metal sulfides to form thiophene ring.<sup>6</sup> The only example of chemical reaction of DA-containing polymers has been reported by Rutherford and Stille.<sup>7</sup> They reacted a DA-containing polythiophene with aniline at 150°C in the presence of CuCl, and obtained a poly(thiophene-*co*-*N*-phenylpyrrol). This reaction cannot be applied to the DA-containing polyesters because the ester bonds do not resist such severe reaction conditions. On the other hand, the halogenation of DA groups takes place under mild conditions where the ester bonds are not broken, and it is expected that polyesters containing controlled amounts of halogens can be obtained.

With respect to the halogenation of butadiyne, up to

four molecules of halogens can be introduced to diacetylenes depending on the reaction conditions. For example, reaction with bromine gives a mixture of products containing four and six bromine atoms,<sup>8</sup> and chlorination at  $-25 \sim -30^\circ\text{C}$  in carbon tetrachloride gives a mixture of hexachlorobutenes,<sup>9</sup> and a fourth chlorine molecule can only be introduced in liquid chlorine with UV irradiation.<sup>10</sup> Patel *et al.*<sup>11</sup> reported that light-sensitive diacetylenes such as 2,4-hexadiynilene-di-(*p*-toluenesulfonate) (1<sub>p</sub>-TS) and *N,N'*-bis(carbon-*n*-butoxymethyl)-1,12-dodeca-5,7-diynylene carbamate (4BCMU), undergo topochemical polymerization in the solid state when exposed to chlorine.

In this paper, halogenations of DA-containing polyesters in the solid state and in solution are discussed.

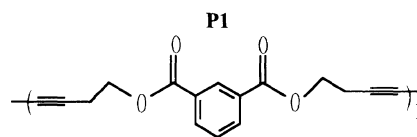
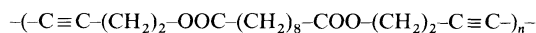
### EXPERIMENTAL

#### Materials

Chloroform was washed twice with water, dried with CaCl<sub>2</sub> and distilled. Other reagents were used as received (Aldrich).

#### Polymer Synthesis

The polymers, poly(octa-3,5-diynylene sebacate) (**P1**) and poly(octa-3,5-diynylene isophthalate) (**P2**) (Scheme 1) were prepared by oxidative coupling of corresponding bis acetylenes according to the literature.<sup>12</sup>



P 2

Scheme 1

<sup>†</sup> Part VIII. S. Fomine, I. Posada, and T. Ogawa, *Macromol. Chem. Phys.*, **196**, 3723 (1995).

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### Measurements

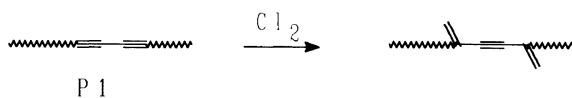
Molecular weights were determined using a Varian 9012 instrument at 30°C in CHCl<sub>3</sub> with a polystyrene standard, a universal column and flow of 1 ml min<sup>-1</sup>. DSC and TGA were performed at a heating rate of 10°C min<sup>-1</sup> under nitrogen using a du Pont 2100 thermal analyzer. FT-IR spectra were taken using a Nicolet 510p spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were taken using a Varian spectrometer at 300 MHz and 75.5 MHz, respectively, in CDCl<sub>3</sub> with TMS as the internal standard.

## RESULTS AND DISCUSSION

### Halogenation in the Solid State

**Chlorination.** In the case of chlorination in the solid state, polymers **P1**, **P2** behaved very differently from one another. **P1** films turned gradually red on exposure to chlorine becoming insoluble in solvents. In the case of **P2** no visible change of the film was observed during the exposure to chlorine and the film was completely soluble in chloroform even after 36 hours. Figure 1 shows FT-IR spectra of **P1** and **P2** films before and after the action of chlorine. Both polymers initially had in their FT-IR spectra absorption bands at 2260, 2205, and 2160 cm<sup>-1</sup>, corresponding to the DA group stretching. After exposure to chlorine a new absorption band appeared in the spectra of both polymers at 2225 cm<sup>-1</sup> corresponding to the new triple bond formed in the polymers by the reaction with chlorine. In the case of **P1**, chlorine obviously induced topochemical cross-polymerization of DA groups (Scheme 2).

The initiation of topochemical polymerization of 1<sub>p</sub>-TS and 4BCMU by chlorine vapor has been reported by Patel.<sup>11</sup> Therefore the absorption band at 2225 cm<sup>-1</sup> corresponds to the stretching of the triple bond of polydiacetylene (PDA) chain. This conclusion is also proved by the insolubility of the exposed polymer film by PDA network formation, and its visible absorption spectrum which is similar to that of the polymer film cross-polymerized by electron beam irradiation.<sup>12</sup>



Scheme 2

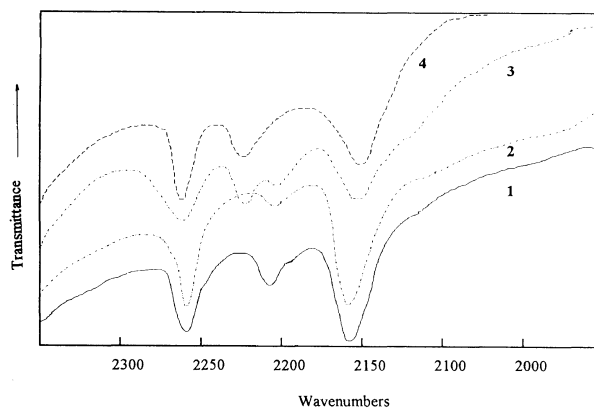
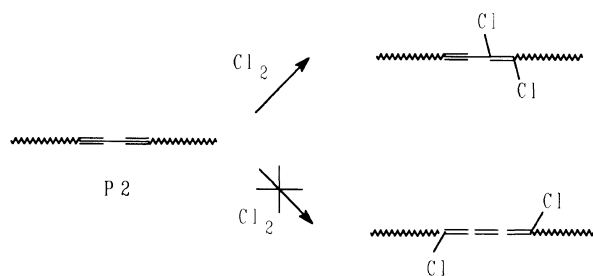


Figure 1. FT-IR spectra of **P1** and **P2** films before (1, 2) and after (3, 4) exposure to chlorine for 36 h, respectively.

In contrast to the case of **P1**, chlorine did not initiate topochemical cross-polymerization of **P2** in the solid state but added to the triple bond to give a soluble partially chlorinated polymer. Therefore, the absorption at 2225 cm<sup>-1</sup> corresponds to the triple bond after 1,2-addition of Cl<sub>2</sub> (Scheme 3). 1,4-Addition can be neglected because the allenic structure has an absorption in IR spectra in the region from 2000 to 1900 cm<sup>-1</sup> which is different from absorption of triple bond.<sup>13</sup>

The different behavior of **P1** and **P2** on chlorination in the solid state can be explained by the difference in morphology. According to X-ray analysis, **P1** films are semicrystalline (degree of crystallinity 40–45%<sup>4</sup>), whereas the films of **P2** are completely amorphous. It is known that topochemical polymerization only takes place in an ordered state.<sup>14</sup> The reaction of polymers **P1** and **P2** with chlorine in the solid state proceeded slowly. Even after 3 days of exposure most of the DA groups still remained in the polymers. In the case of the crystalline **P1**, topochemical polymerization initiated by chlorine addition appears to proceed more rapidly than the penetration of chlorine molecules into the film.

**Bromination.** The reaction of **P1** with bromine in the solid state differs dramatically from that with chlorine. No topochemical cross-polymerization of DA groups took place on exposure of **P1** film to bromine vapor, but relatively fast addition reaction of bromine occurred instead, with the complete disappearing of triple bonds after 8 hours of exposure. As can be seen in Figure 2, diacetylene stretching completely disappeared after 4 hours and absorption of separate triple bond arose at 2225 cm<sup>-1</sup> which corresponded to the product of 1,2-addition of one Br<sub>2</sub> molecule to DA group. After 8 hours no triple bond stretching could be detected. No change of IR spectra was observed on further exposure



Scheme 3

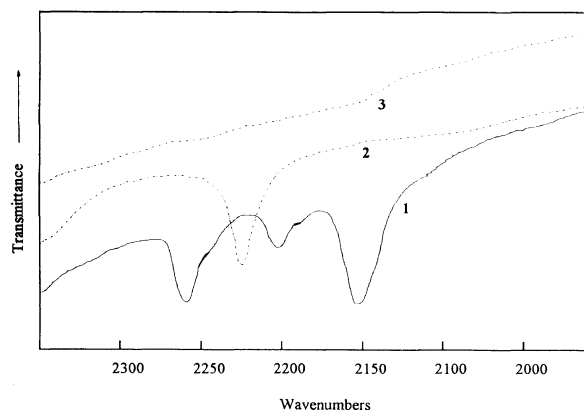


Figure 2. FT-IR spectra of **P1** film before (1) and after exposure to bromine vapor for 4 h (2) and 8 h (3).

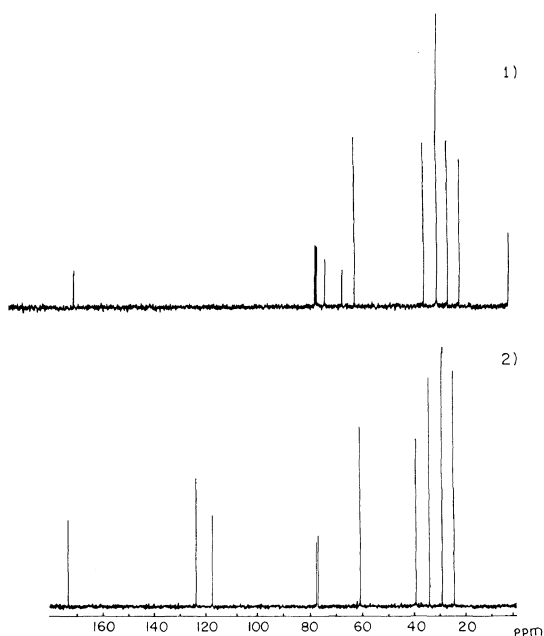


Figure 3.  $^{13}\text{C}$  NMR spectra of **P1** before (1) and after (2) 30 h exposure to bromine vapor.

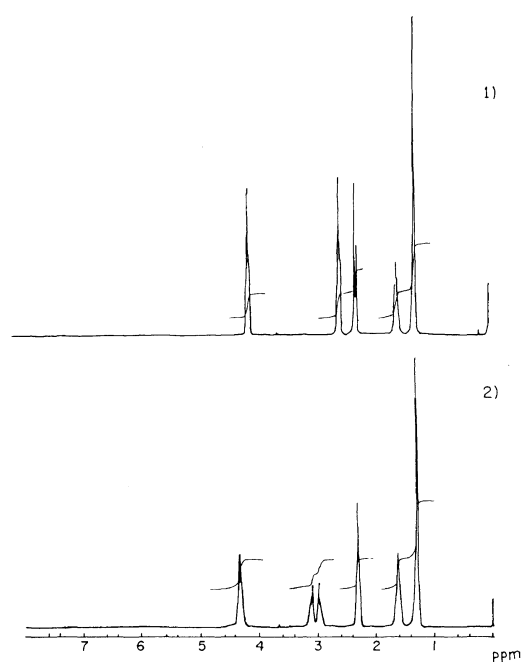
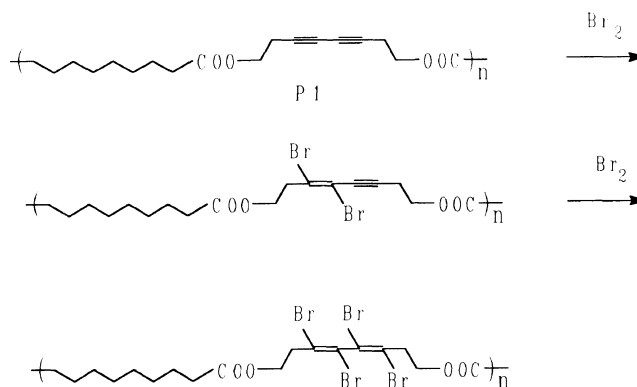


Figure 4.  $^1\text{H}$  NMR spectra of **P1** before (1) and after (2) 30 h exposure to bromine vapor.

of polymer film to bromine vapor.

Figure 3 shows  $^{13}\text{C}$  NMR spectra of **P1** before and after 30 hours exposure to bromine vapor. The following changes could be seen in the spectra after the bromination: two signals of diacetylene carbons at 73.52 and 66.55 ppm disappeared and two new signals at 123.6 and 117.4 ppm arose which corresponded to the olefinic carbons. In the aliphatic region two signals of  $sp^3$  carbons at 19.82 and 61.57 ppm ( $\text{CH}_2\text{-C}\equiv$  and  $\text{-CH}_2\text{-O-}$ ), respectively, disappeared and two new signals arose at 39.24 and 60.80 ppm.

Figure 4 shows  $^1\text{H}$  NMR spectra of **P1** before and after the 30 hours exposure to bromine vapor. The proton signals of octamethylene spacer (2.31 ppm, t, 4H,

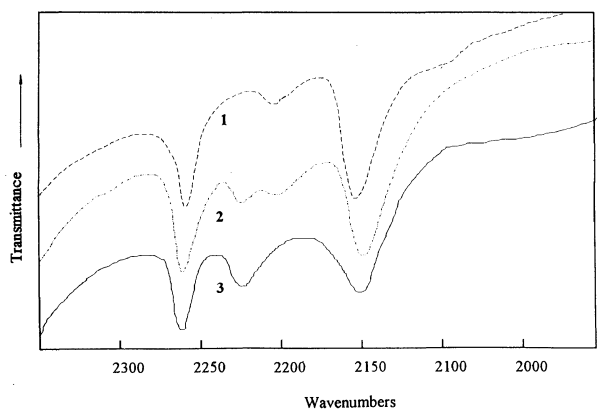


Scheme 4

1.61 ppm, t, 4H, 1.30, s, 8H) showed no change after bromination, implying that bromine was not incorporated into this part of polymer chain by free radical substitution reaction. Two triplets at 2.59 and 4.16 ppm, corresponding to the protons of  $\text{CH}_2\text{-C}\equiv$  and  $\text{-CH}_2\text{-O-}$  groups, respectively, disappeared and two new multiplets with the same number of protons arose at 4.40–4.25 and 3.19–2.91. These data prove that the following sequence of chemical reactions takes place during the bromination of **P1** in the solid state (Scheme 4).

After 4 hours of bromination, most DA groups added one bromine molecule which corresponded to the appearance of a new absorption band at  $2225\text{ cm}^{-1}$  and disappearance of DA stretching in FT-IR spectra. The final product of the bromination should contain four bromine atoms per repeating unit. Two signals at 123.6 and 117.4 ppm in  $^{13}\text{C}$  NMR spectra of the product of bromination correspond to two different carbons of tetrabromobutadiene moiety, and two new signals in aliphatic region at 39.24 and 60.80 ppm, belonged to the carbons  $\text{-CBr=CBr-CH}_2\text{-CH}_2\text{-O-}$ , and  $\text{-CBr=CBr-CH}_2\text{-CH}_2\text{-O-}$ , respectively. Other signals did not change their positions, indicating that no additional bromine atom was incorporated in the polymer chain by free radical substitution reaction. New signals in  $^1\text{H}$  NMR spectra of the brominated **P1** at 4.40–4.25 and 3.19–2.91 ppm, belonged to the protons  $\text{-CBr=CBr-CH}_2\text{-CH}_2\text{-O-}$ , and  $\text{-CBr=CBr-CH}_2\text{-CH}_2\text{-O-}$ , respectively. Elemental analysis data also proved the structure of the bromination product. Bromine content calculated for **P1** containing four bromine atoms per repeat unit was 51.2% which agrees reasonably well with experimental data (48.51%).

The difference between chlorination and bromination of **P1** in the solid state may be explained by the difference in size of chlorine and bromine atoms. In the case of chlorination the initial addition of chlorine to the DA groups of polymer only slightly distorts the crystalline structure of polymer film, still making possible the chlorine-initiated topochemical cross-polymerization of DA-groups which proceeds rapidly in the surface layer of the film, thus preventing further addition reaction of chlorine to DA-groups. The addition of bromine to DA groups of **P1** destroys completely the crystalline structure of the polymer film (bromination product is a rubber like amorphous polymer) facilitating further addition of bromine and making impossible halogen initiated topochemical cross-polymerization of DA-groups.

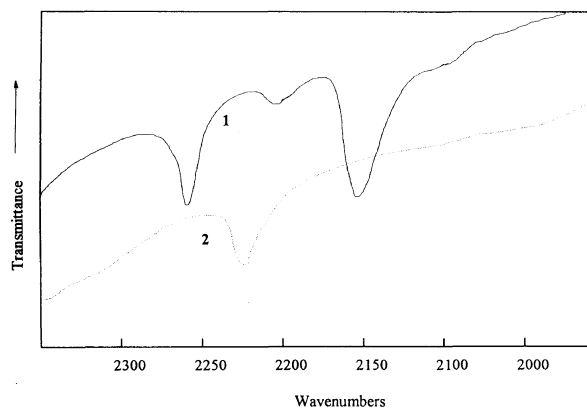


**Figure 5.** FT-IR spectrum of **P2** film before (1) and after exposure to bromine (1) and chlorine (2) for 30 h.

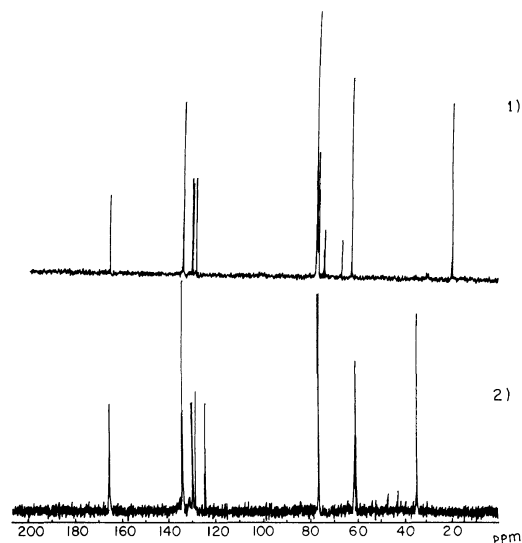
The solid state bromination of **P2** film was very slow compared with **P1** film. The reason for this difference cannot be explained exactly, but it seems to be due to the difference in morphology. The DA groups of **P1** are more concentrated locally (in crystalline regions) while those of amorphous **P2** are dispersed. The rate of penetration of bromine molecules in the polymer is a slow process, but the bromination of DA is a faster reaction. More studies are necessary to find the cause for this reactivity difference. Figure 5 shows FT-IR spectra of **P2** film treated by bromine vapor for 30 hours. The spectra of the film chlorinated for 30 hours is also shown for comparison. The spectrum of brominated film resembles that of chlorinated film with the only difference that the absorption band at  $2225\text{ cm}^{-1}$  corresponding to the triple bond of  $-\text{CBr}=\text{CBr}-\text{C}\equiv\text{C}-$  group, is less intense and the absorption band at  $2205\text{ cm}^{-1}$  of the DA group is still seen in the spectra. This agrees with the fact that chlorine is more active than bromine in reactions of electrophilic addition to the multiple carbon-carbon bonds.

#### Halogenation in the Solution

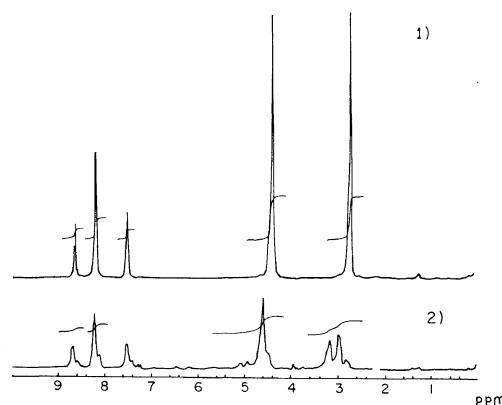
**Chlorination.** Unlike chlorination in the solid state, **P2** reacts readily with chlorine in chloroform solution. Figure 6 shows FT-IR spectra of **P2** before and after 30 hours of chlorination in chloroform solution. The absorption bands corresponding to DA stretching at  $2260$ ,  $2205$ , and  $2160\text{ cm}^{-1}$  disappeared completely after 30 hours of chlorination. However, in contrast to bromination in the solution, the absorption band at  $2225\text{ cm}^{-1}$  corresponding to the partially chlorinated DA groups ( $-\text{CCl}=\text{CCl}-\text{C}\equiv\text{C}-$ ) still could be seen in the spectra even after 30 hours of chlorination. This contradiction between the experimental results and the reactivities of chlorine and bromine could be explained by the different transition dipole moments of the stretching of the triple bonds of  $-\text{CCl}=\text{CCl}-\text{C}\equiv\text{C}-$  and  $-\text{CBr}=\text{CBr}-\text{C}\equiv\text{C}-$  groups. The transition dipole moment of the former is greater than that of the latter owing to the greater electronegativity of chlorine. This makes the absorption corresponding to the stretching of the triple bond of  $-\text{CCl}=\text{CCl}-\text{C}\equiv\text{C}-$  group more intense than that of  $-\text{CBr}=\text{CBr}-\text{C}\equiv\text{C}-$  group. This assumption is also supported by the data of NMR spectroscopy. Figure 7 shows  $^{13}\text{C}$  NMR spectra of **P2** before and after



**Figure 6.** FT-IR spectra of **P2** before (1) and after (2) its chlorination in solution for 30 h.

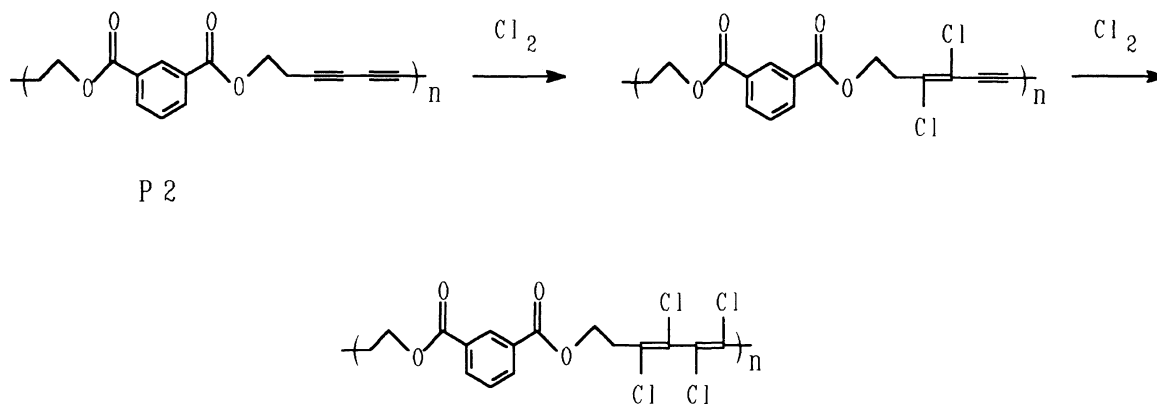


**Figure 7.**  $^{13}\text{C}$  NMR spectra of **P2** before (1) and after (2) 30 h chlorination in chloroform solution.



**Figure 8.**  $^1\text{H}$  NMR spectra of **P2** before (1) and after (2) 30 h chlorination in chloroform solution.

30 hours chlorination in chloroform solution. The signals at 73.39 and 66.83 ppm, corresponding to the carbons of the DA group disappeared after the chlorination and no other signal of the triple bond could be detected. In the region of the olefinic carbons appeared two new signals at 124.5 and 132.8 ppm assigned to the carbons of  $-\text{CCl}=\text{CCl}-\text{CCl}=\text{CCl}-$  group. In the region of aliphatic protons two signals corresponding to  $\equiv\text{C}-\text{CH}_2-$  and  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{C}\equiv$  carbons at 19.90 and 62.60 ppm,



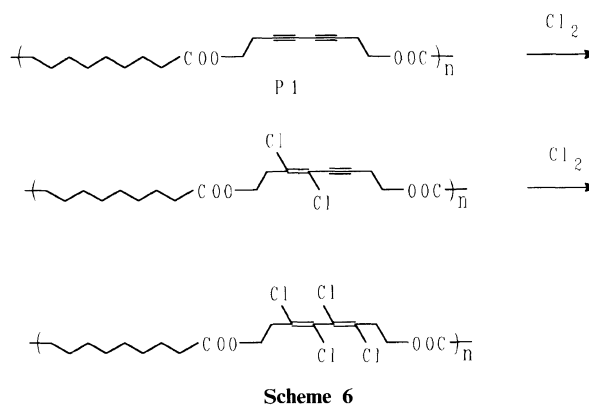
Scheme 5

respectively, disappeared after chlorination and two new signals could be detected at 35.06 and 61.26 corresponding to  $-\text{CCl}=\text{CCl}-\text{CH}_2-$  and  $\text{CCl}=\text{CCl}-\text{CH}_2-\text{CH}_2-$  carbons, respectively.  $^1\text{H}$  NMR spectra of **P2** before and after 30 hours chlorination in chloroform solution are shown in Figure 8. The signals of the protons of  $\equiv\text{C}-\text{CH}_2-$  and  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{C}\equiv$  (2.7–2.9 and 4.3–4.6 ppm, respectively) disappeared and new signals arose at 3.00–3.20 and 4.6–4.8 ppm, which correspond to  $-\text{CCl}=\text{CCl}-\text{CH}_2-$  and  $\text{CCl}=\text{CCl}-\text{CH}_2-\text{CH}_2-\text{O}$  protons, respectively. The chlorination of **P2** in solution, thus can be presented as follows (Scheme 5); which was also confirmed by elemental analysis (chlorine content calculated for  $(\text{C}_{16}\text{H}_{12}\text{O}_4\text{Cl}_4)_n$  was 34.6%, found 34.8%).

Similar to the case of **P2**, four chlorine atoms added to **P1** per repeating unit when chlorinated in chloroform (Scheme 6), which was confirmed by FT-IR, and NMR spectroscopy. Figure 9 presents FT-IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectra of **P1** chlorinated in chloroform solution for 30 hours. The FT-IR spectrum resembles that of the chlorinated **P2**, and  $^{13}\text{C}$  NMR spectra exhibited two signals of two different carbons of tetrachlorobutadiene moiety (124.6 and 132.9 ppm). Two new signals arising in the aliphatic region at 35.00 and 61.30 ppm were similar to those of the chlorinated **P2**. The spectra no longer showed the DA peaks at 73.39 and 66.83 ppm and all signals of octamethylene spacer did not show any change after the chlorination. The structure of the product of chlorination was confirmed also by the elemental analysis. Chlorine content calculated for the product containing four chlorine atoms per repeat unit was 31.8%, and the elemental analysis data gave 31.7% of chlorine in the chlorination product.

**Bromination.** The bromination of **P1** in solution showed no difference from that in the solid state. The spectra (FT-IR,  $^{13}\text{C}$  NMR, and  $^1\text{H}$  NMR) of the final product of the bromination (30 hours) in solution was similar to that of the bromination in the solid state suggesting that the same product was formed in both cases (Scheme 4).

Unlike the reaction in the solid state, **P2** reacted readily with bromine in chloroform solution adding four bromine atoms per repeating unit. After 30 hours bromination all peaks corresponding to DA groups and triple carbon-carbon bonds disappeared from FT-IR



Scheme 6

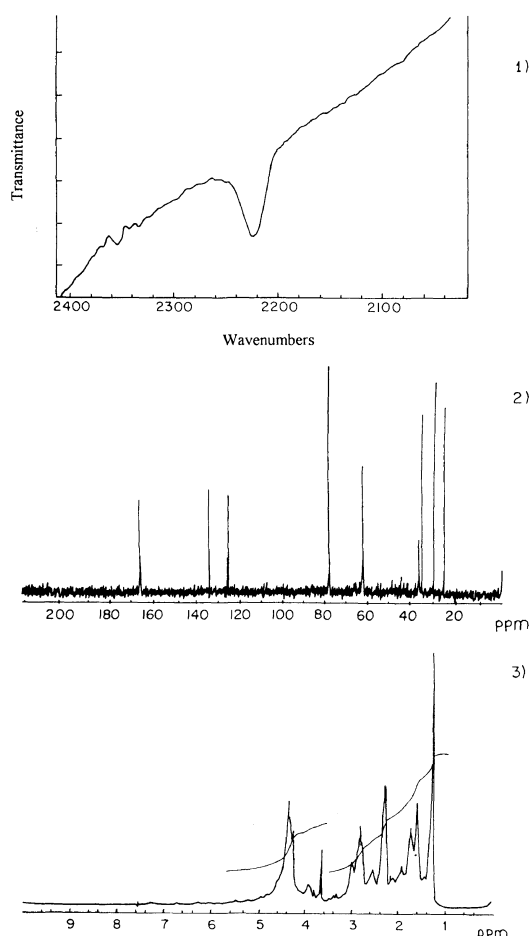
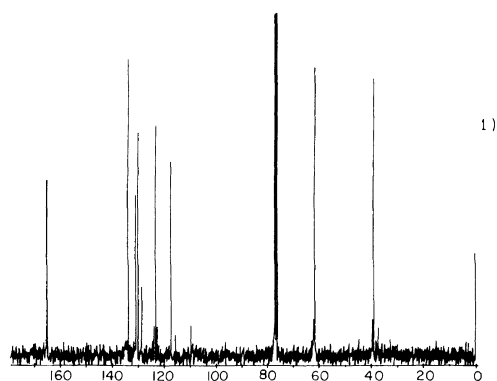
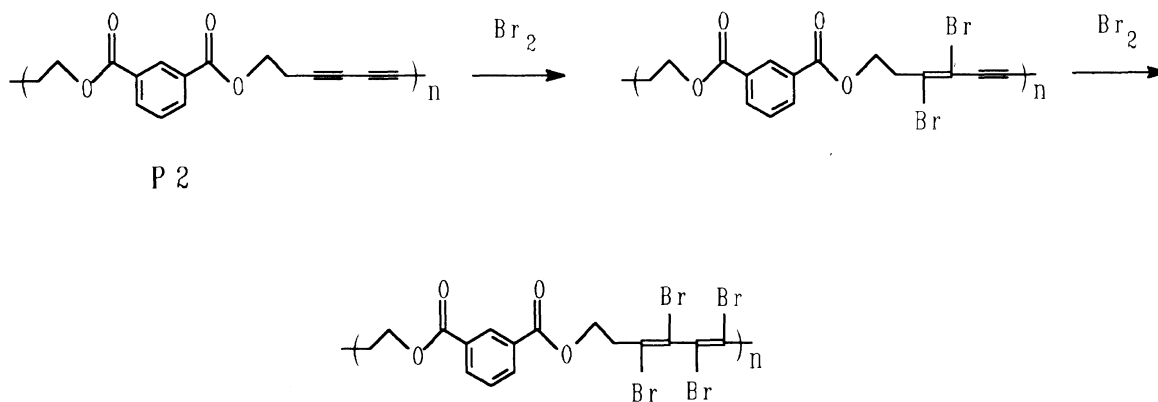


Figure 9. FT-IR (1),  $^1\text{H}$  NMR (2), and  $^{13}\text{C}$  NMR spectra (3) of **P1** chlorinated in chloroform solution for 30 h.



1)

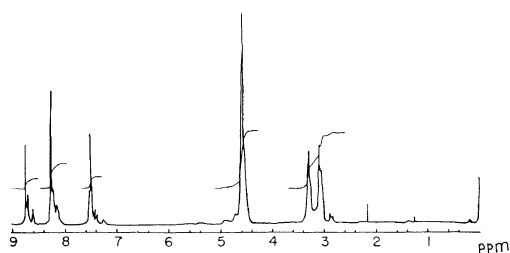


Figure 10.  $^{13}\text{C}$  NMR (1) and  $^1\text{H}$  NMR spectra (2) of **P2** after 30 h bromination.

spectra. Figure 10 shows  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectra of **P2** after 30 hours bromination. The signals of DA carbons disappeared after bromination and new signals of tetrabromobutadielylene group arose at 117.6 and 123.5 ppm. The signals of  $-\text{CBr}=\text{CBr}-\text{CH}_2-\text{CH}_2-\text{O}-$ , and  $-\text{CBr}=\text{CBr}-\text{CH}_2-\text{CH}_2-\text{O}-$  carbons arose at 39.26 and 61.9 ppm instead of those of unbrominated polymer at 19.82 and 61.57 ppm ( $\text{CH}_2-\text{C}\equiv$  and  $-\text{CH}_2-\text{O}-$ ), respectively. The  $^1\text{H}$  NMR spectrum of the product of bromination of **P2** was similar to that of chlorinated **P2** and confirmed the structure of the product of the bromination presented in Scheme 7. Elemental analysis data also agreed reasonably well with the structure shown in the Scheme 7 (bromine content calculated for  $(\text{C}_{16}\text{H}_{12}\text{O}_4\text{Br}_4)_n$  was 54.4%, found 52.2%). The bromination and chlorination in the solid state and solution converted **P1** to **P1** totally amorphous rubber like materials owing to the incorporation of four bulky halogens. As an example, Figure 11 shows DSC curves of **P1** film before and after exposure to bromine vapor. **P1** shows a melting transition at 122°C and an exotherm

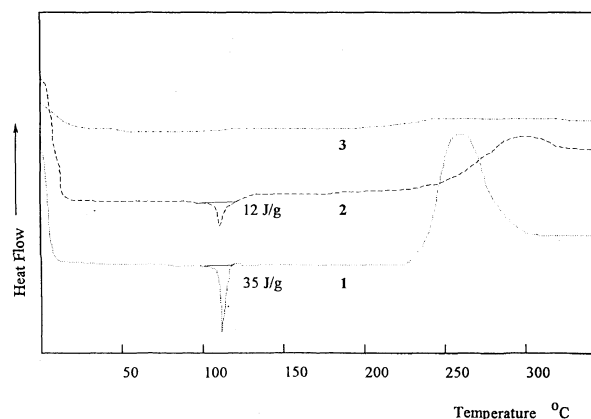


Figure 11. DSC curves of **P1** film before (1) and after the exposure to bromine vapor for 15 min (2) and 15 h (3).

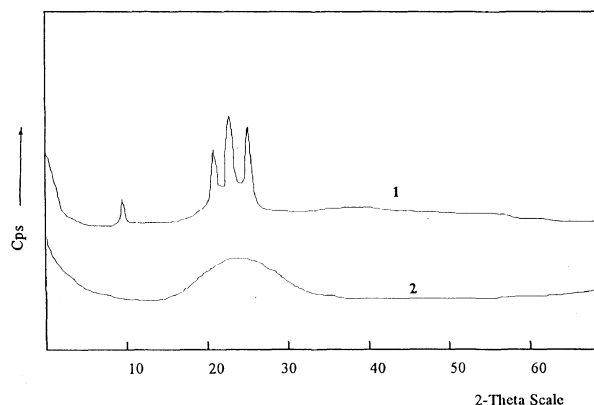


Figure 12. X-Ray diffractograms of **P1** before (1) and after 15 h exposure to bromine vapor (2).

in the region of 220–280°C which is due to the thermal cross-linking of DA groups. It can be seen from the heats of melting that even after 15 min of exposure, the degree of crystallinity of **P1** decreased significantly and the sample exposed to bromine vapor for 15 hours showed no melting transition and no exotherm, due to the consumption of DA groups. These data were also confirmed by X-ray diffractometry. Figure 12 shows X-ray diffractograms of **P1** before and after 15 hours exposure to bromine vapor. It can be seen that **P1** became totally amorphous after the bromination. The thermostability of the polymers did not change appreciably by halogenation. Both **P1**, **P2** and their products of halogenation showed 5% weight loss at around 300°C.

$M_w$  of **P1** and **P2** before halogenation were 66000 and 80200 with polydispersity index of 2.9 for both. The polymers brominated in chloroform solution for 30 hours showed  $M_w$  of 67000 and 66000 for **P1** and **P2** with a polydispersity index of 3.4. The products of chlorination in solution showed  $M_w$  of 63000 and 59000 with polydispersity index of 3.1 and 3.5 for **P1** and **P2**, respectively. In FT-IR and  $^{13}\text{C}$  NMR spectra of halogenated polymers did not contain any detectable signal ascribable to the end groups of degraded polymer. These data imply that relatively little degradation of the polymers occur during halogenation.

## CONCLUSIONS

Halogenation reactions of DA-containing polyesters were studied in the solid state and chloroform solution. In solid state chlorine induced the solid-state topochemical cross-polymerization of DA groups of semi-crystalline polymer **P1**, but in the case of amorphous polymer **P2**, chlorine added to DA bonds giving partially chlorinated polymer. However, this reaction was slow in the solid state.

In the case of bromination in the solid state, **P1** gave tetrabromobutadiene-containing polyesters by adding four bromine atoms per repeat unit. **P2** film was less affected by bromine giving, partially brominated product.

Halogenation in chloroform solution gave tetrahalobutadiene-containing polymers by adding four halogen atoms per repeat unit for both polymers. The bromination of **P1** (in the solid state and solution) and chlorination in the solution led to total amorphization of the polymer with only moderate degradation of the

polymers. These halogenated polymers lost their weight by 5% at 300°C.

This work shows that interesting novel polymers with various amount of halogens and cross-linkable DA units can be obtained from DA-containing polymers.

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