

A DSC STUDY OF PHOTOPOLYMERIZATION OF POLYESTERS CONTAINING CONJUGATED DIACETYLENES

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Abstract The photopolymerization of two kinds of prepolymers containing conjugated diacetylene (PDA-6 and PDA-12) was investigated using DSC. By measuring the endothermic enthalpy of the prepolymers after different UV-irradiation times, the polymerizations were found to follow the first-order rate law which agreed with the results of other investigators using a different method. The endothermic enthalpy measurements of PDA-6 and PDA-12 before UV-irradiation precluded the possibility that the decrease of endothermic enthalpy was caused by thermal polymerization.

Keywords Diacetylene-containing polyesters, DSC, Enthalpy

INTRODUCTION

It has been demonstrated that the diacetylene functionality can be incorporated into the repeat structure of a polymer backbone and that such polymers can undergo crosslinking-polymerization on exposure to ultraviolet radiation or by annealing at elevated temperatures^[1] (Scheme 1). Most research on poly(diacetylenes) (PDAs) has been concentrated on properties such as their nonlinear optical properties^[2], thermochromic properties^[3], and highly anisotropic mechanical properties^[4]. Since PDAs contain the IR inactive centrosymmetric diacetylenes, it is difficult to study the polymerization of PDAs with IR. On the other hand, since the crosslinking-polymerized PDAs are usually insoluble in common organic solvents, it is also difficult to investigate the polymerization by NMR. Therefore, relatively little work has been devoted to the study of the polymerization of PDAs. Wegner^[5] and Patil^[6] investigated the UV polymerization of poly(diacetylenes) using a monomer extraction method. But there are certain problems with this method^[7]. At low conversions this procedure tends to underestimate the polymer content owing to inevitable dissolution of polymer in the extraction solvent. At high conversions, the procedure tends to overestimate the polymer content owing to trapping of monomer in the polymer crystal lattice. Rubner and coworkers^[8] mentioned that the degree of conversion can be estimated from DSC measurements of the melting endotherm, but they did not provide any details of the experiment. In this paper, we describe the DSC study of photopolymerization of polyesters containing conjugated diacetylenes by measuring the endothermic enthalpy of polyesters after various UV-irradiation times.

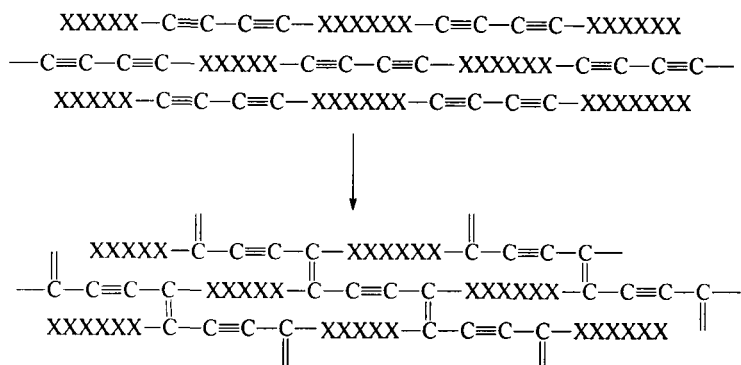
EXPERIMENTAL

Monomer and Prepolymer Preparations

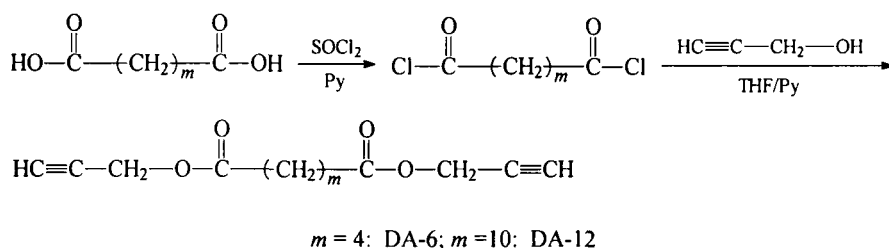
The monomers, dipropargyl 1,12-dodecanedioate (DA-12) and dipropargyl adipate (DA-6), were prepared from the diacid dichlorides and propargyl alcohol. The synthetic route is illustrated in Scheme 2.

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Scheme 1 Solid-polymerization of polymer containing DAs



Scheme 2 The synthesis of monomers

As an example, the preparation of DA-6 is described. 2.464 g of propargyl alcohol was dissolved in 10 mL THF while a solution of 3.66 g adipoyl chloride in 5 mL pyridine was added slowly. After 4–6 h, the mixture was poured into acidified water (pH = 1). The precipitate was filtered and purified by recrystallization from ethanol. Yield: 50%. $T_m = 34^\circ\text{C}$ (for DA-6) and $T_m = 38^\circ\text{C}$ (for DA-12).

The DA-containing prepolymers were prepared by oxidative coupling reaction^[9] of these dipropargyl monomers. They are white compounds when freshly synthesized and become orange if exposed to UV radiation, which means that they are photosensitive. The chemical structures of the prepolymers are shown in Fig. 1.

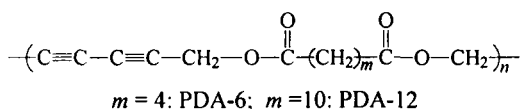


Fig. 1 The chemical structures of DA-containing prepolymers

Prepolymer Characterization

The molecular weights of prepolymers were measured by GPC with polystyrene standards in THF by using a Waters 2410 instrument. Differential scanning calorimetry (DSC) was performed with a Mettler FP90 instrument equipped with DSC modules. Melting points were taken as the maximum in the endothermic peak. For DSC, samples were run at 20 K/min in nitrogen. Raman scattering experiments were performed at room temperature on a Renishaw-1000 Raman instrument. Incident radiation of 632.8 nm at about 0.2 mW was provided by a He-Ne laser. After the Raman measurement, the prepolymer samples did not show any change of color, which means there is no obvious crosslinking-polymerization or other side reactions occurring during the experiment.

Photopolymerization Studies of PDAs

The prepolymer was dissolved in purified chloroform to obtain a 0.03 wt% polymer solution. The solution was

poured into a DSC cell and the solvent was allowed to evaporate. The final removal of the solvent was achieved in vacuum.

Table 1. Some properties of DA-containing prepolymers

Samples	M_n	M_w	Endotherms ^a (°C)	Exotherms (°C)	T_d^b (°C)
PDA-6	2610	3310	70.9	199.0	299
PDA-12	3969	5206	80.5	216.7	300

^a Values of the first heating process

^b By which 5% weight loss was observed

Photopolymerization was conducted using Mettler FP 90 equipped with a UV lamp to select UV radiation of a specific wavelength (254 nm). The UV lamp (8 W) was kept at a distance of 11 cm from the film. Prior to photopolymerization, the sample was heated to above melting point and cooled to room temperature to ensure uniformity in the film.

The DSC investigation of photopolymerization was monitored by measuring the endothermic melting enthalpy of the sample, which had been exposed to UV irradiation for different lengths of time. After the film was exposed to UV for a certain period of time, the endothermic enthalpy was measured by DSC. The film was then cooled in nitrogen to room temperature and exposed to UV for another desired period of time. The endothermic enthalpy of the sample was measured again.

The endothermic enthalpy of the original unirradiated DA-containing prepolymers was also measured as a control.

Analysis

According to Baughman^[10], the solid-state photopolymerization of monomer containing diacetylene occurs only in the solid phases of the monomer molecules (the prepolymers in this study) which satisfy certain packing requirements, i.e., the reactive carbon centers on adjacent molecules are no more than 0.4 nm apart and the molecular axis makes an angle of about 45° with the line joining the two centers. This implies that the photopolymerization occurs only in certain “crystals” of the DA-containing polymers. Because the crystallinity of these “crystals” and the melting enthalpy will decrease with photopolymerization, therefore, by measuring the melting endotherm after different times of photo-irradiation, we can get a conversion (i.e., extent of photopolymerization of the diacetylene groups in the prepolymers) versus time curve if Eq. (1) is applied:

$$\text{Conversion (\%)} = \left(1 - \frac{\Delta H_t}{\Delta H_0} \right) \times 100\% \quad (1)$$

where ΔH_0 is the area of the DSC melting peak or enthalpy of the original unirradiated sample, ΔH_t is the melting peak area or enthalpy of the sample after exposure to UV irradiation for time t .

RESULTS AND DISCUSSION

The DSC scans of PDA-6 and PDA-12 are shown in Fig. 2. The endotherms of PDA-6 and PDA-12 at about 70°C result from the melting of the crystals, while the exothermic transitions at about 200°C are due to a combination of the thermally induced liquid-phase polymerization and the thermal degradation of the samples at such high temperatures. A similar observation was made by Rubner on polyurethane-diacetylene segmented copolymers^[11]. Thus, this study was focused on the DSC peak at about 70°C.

It is notable that the endothermic peak of PDA-6 split into two when PDA-6 was heated for the second time: one centered at 70.9°C and the other at 62.6°C. If the sample was kept at 65°C for 20 min, cooled to room temperature in nitrogen, and heated for the third time, the peak at 62.6°C will diminish and the peak at 70.9°C will move to a slightly higher temperature (72.2°C) (Fig. 3). This type of multimelting has been observed for many other polymers including liquid crystalline polymers and non-liquid crystalline polymers^[12, 13]. Thus, the

two peaks are regarded as a whole in the following calculations. The inaccuracy in the enthalpy measurement arising from this combination will introduce an error in the results of this study. This multimelting was not observed for PDA-12.

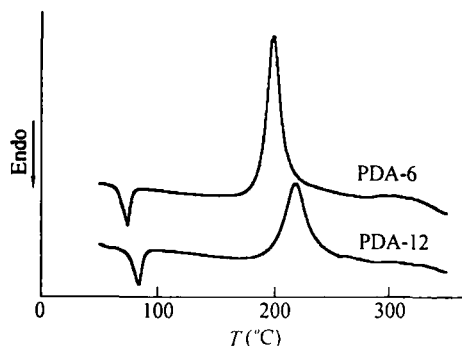


Fig. 2 DSC thermograms of PDA-6 and PDA-12

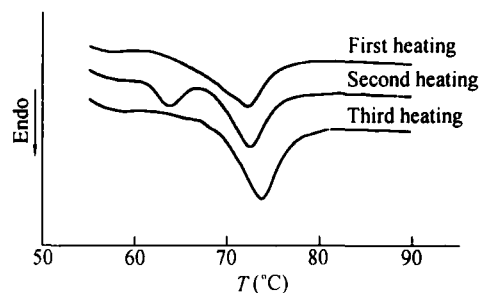


Fig. 3 DSC thermograms of PDA-6 from different heat/cool cycles

In order to preclude the possibility of changing the melting enthalpy with heating and cooling in the DSC study, the two samples were heated to above their melting temperatures and heat-treated at that temperatures (90°C for PDA-6, 100°C for PDA-12) for different lengths of time. The samples were then studied by DSC. The results are shown in Fig. 4. We observed that the endothermic peaks of PDA-6 remain almost unchanged, which implies that repeated heating and cooling do not affect the melting of the two prepolyesters. In other words, the melting enthalpy change observed in the following experiments is not caused by repeated heatings and coolings, but is caused by the UV induced polymerization (crosslinking).

Figure 5 shows the DSC thermograms of PDA-6. On exposure to UV irradiation, the endothermic peak centered at 70.9°C quickly vanishes, while the endothermic peak centered at 62.6°C remains almost unchanged and then diminishes until the UV-irradiation time reaches about 500 s. This implies that the UV induced polymerization will affect first the formation of the more stable (larger in size and with less defects) crystals. The formation of the less stable crystals is less affected and becomes impossible only after a long time of irradiation. A slower decrease of the peak size with irradiation is observed for PDA-12 (not shown by a figure).

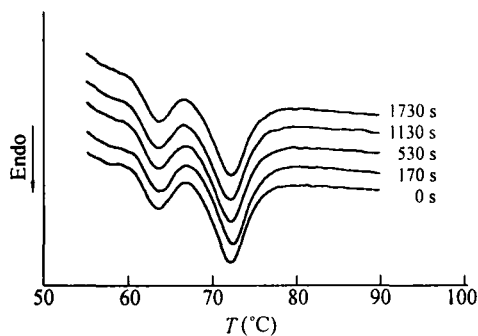


Fig. 4 DSC heating curves of PDA-6 after different time of annealing at 90°C

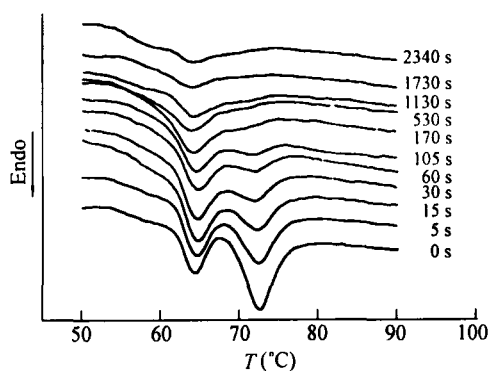


Fig. 5 DSC thermograms of PDA-6 after different time of UV-irradiation

Figure 6 is a plot of conversion as a function of irradiation time. Figure 7 shows the plots of $\ln(1/(1-\text{conv.}))$ versus irradiation time. When the conversion was low (40%–50%), the plots follow a linear relationship, which means that the reactions follow the first-order rate law. The slopes for these plots at low conversion are $1.80 \times 10^{-2} \text{ s}^{-1}$ (for PDA-6) and $3.2 \times 10^{-3} \text{ s}^{-1}$ (for PDA-12), respectively. PDA-6 has been studied by Patil^[6] by means of

the monomer extraction. The value obtained by him was $k = 1.033 \times 10^{-2} \text{ s}^{-1}$. Therefore we consider that the DSC method used in this study and the monomer extraction method can give similar results. The polymerization rate of PDA-12 is lower than that of PDA-6 which is probably due to the lower concentration of the diacetylene groups in the PDA-12.

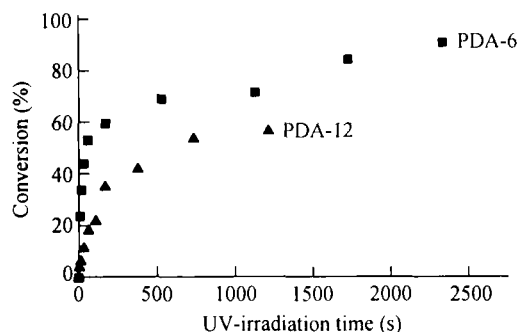


Fig. 6 Plots of conversion versus the UV-irradiation time

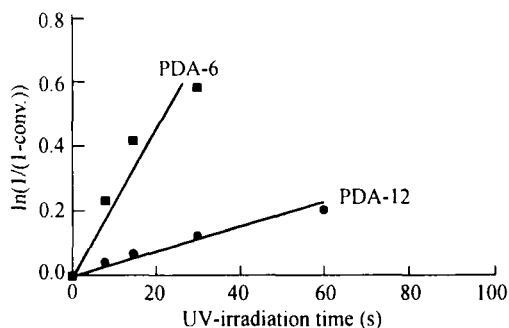


Fig. 7 Plots of $\ln(1/(1-\text{conv.}))$ versus UV-irradiation time
The conversion was below 50%.

Figure 8 displays the room temperature Raman spectra of the original and the 60 s UV-irradiated PDA-6s. The band around 2264 cm^{-1} is the characteristic Raman absorption of diacetylenes. After 1,4 addition polymerization by UV-irradiation, the Raman bands of the carbon-carbon double bond and the triple bond vibration of the conjugated backbone are found at 1531 and 2135 cm^{-1} , respectively. The band around 2264 cm^{-1} still exists because of incomplete polymerization, but the area under the peak becomes smaller. Since the absorption at 1736 cm^{-1} ($-\text{C}=\text{O}$) remains unchanged, the conversion of polymerization can be obtained by comparing the area of bands at 2264 cm^{-1} with that of the bands at 1736 cm^{-1} before and after UV-irradiation. After UV-irradiation for 60 s, the conversion found by this comparison is 37%, while the conversion calculated from DSC is 51%.

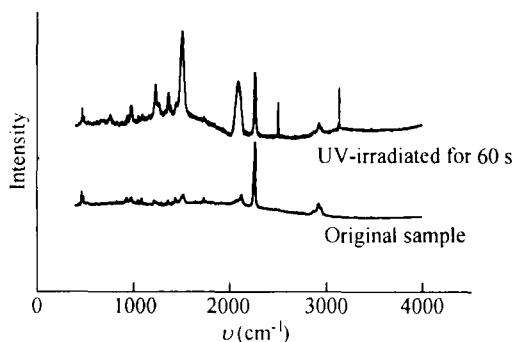


Fig. 8 Raman spectra of PDA-6

As we know, the percentage decrease of endothermic enthalpy is not the same as the conversion of the polymerization reaction. Since crosslinking polymerization lowers the crystallizability of the polymer, the polymer may become even uncrystallizable far before the completion of the polymerization. Thus, the conversion calculated from the melting enthalpy will be higher than the true conversion as more precisely determined by Raman spectroscopy.

In summary, we investigated the photopolymerization of DA-containing polyesters by DSC, and compared the results with those obtained from the monomer extraction method and from Raman spectroscopy. The

comparative results from DSC and the monomer extraction agree well, but both give a higher extent or a faster rate of polymerization than Raman spectroscopy. Nevertheless, because the DSC method is very convenient, it is useful for monitoring the polymerization of certain monomer or prepolymers provided that the material of concern is crystallizable and its melting point is far below the thermal polymerization temperature or other thermal reaction temperatures.

REFERENCES

- 1 Thakur, M.K. and Lando, J.B., *Macromolecules*, 1983, 16: 143
- 2 Carter, G.M., Chen, Y.J. and Tripathy, S.K., *Appl. Phys. Lett.*, 1983, 43: 891
- 3 Hammond, P.T. and Rubner, M.F., *Macromolecules*, 1997, 30: 5773
- 4 Galiotis, C., Read, R.T., Yeung, P.H. and Young, R.J., *J. Polym. Sci., Polym. Phys. Ed.*, 1984, 22: 1589
- 5 Wegner, G., *Makromol. Chem.*, 1971, 145: 85
- 6 Patil, A.O., Deshpande, D.D. Talwar, S.S. and Biswas, A.B., *J. Polym. Sci., Polym. Phys. Ed.*, 1981, 19: 1155
- 7 Chance, R.R. and Sowa, J., *J. Am. Chem. Soc.*, 1977, 99: 6703
- 8 Hammond, P.T. and Rubne, M.F., *Macromolecules*, 1995, 28: 795
- 9 Chen, X.F., Bai, Y.W., Ma, Y.G., Wang, C.H., Wan, X.H. and Zhou, Q.F., *Chin. J. Polym. Sci.*, 1999, 17: 193
- 10 Baughman, R.H., *J. Appl. Phys.*, 1972, 43: 4362
- 11 Rubner, M.F., *Macromolecules*, 1986, 19: 2114
- 12 Holdsworth, P.J. and Turner-Jones, A., *Polymer*, 1971, 12: 195
- 13 Griffin, A.C. and Havens, J., *J. Polym. Sci., Polym. Phys. Ed.*, 1981, 19: 951