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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Usanmaz, A. and Baytar, N.(1998) 'Topotactic Solid-State Polymerization of Acenaphthylene by Radiation', *Journal of Macromolecular Science, Part A*, 35: 1, 161 – 173

To link to this Article: DOI: 10.1080/10601329808001968

URL: <http://dx.doi.org/10.1080/10601329808001968>

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TOPOTACTIC SOLID-STATE POLYMERIZATION OF ACENAPHTYLENE BY RADIATION

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Key Words: Acenaphthylene, Radiation-induced Polymerization, Topotactic Polymerization, Solid-state Polymerization

ABSTRACT

The radiation-induced solid-state polymerization of acenaphthylene was carried out under vacuum at room temperature. The monomer and obtained polymer samples were investigated by UV, FTIR, DSC, TG, and powder X-ray diffraction methods to characterize the polymer and elucidate the polymerization mechanism. The polymer samples were crystalline with melting points ranging in 380-390°C interval. Polymerization takes place through vinyl groups by a radical mechanism and crystal structure of monomer and polymer studied by powder X-ray diffraction were quite similar. The space group for both were $P2_21_2$ and cell parameters: $a = 784.2(6)$, $b = 798.1(6)$, $c = 1417.0(1)$ pm for monomer, and $a = 791.7(8)$, $b = 803.8(7)$, $c = 1431.0(1)$ pm for polymer. The similarity of crystal structures shows a topotactic polymerization of monomer.

INTRODUCTION

Acenaphthylene, $C_{12}H_8$, is a crystalline aromatic vinyl monomer that has a bulky naphthalene group *cis*-disubstituted on the carbon-carbon double bond. The melting point given in the literature is 92-93°C and the boiling point is 103-105°C.

Acenaphthylene polymerization has been reported to take place easily by radical, cationic, anionic, electroinitiation, thermal, and radiation initiators [1-11]. The ease of polymerization of this monomer can be attributed to the fact that the conversion of the double bond in monomer to a single bond in the polymer relieves considerable strain in the five-member ring [12]. The detail solid-state polymerization of acenaphthylene by X-ray radiation was carried out for the first time by Moacanin and Rembaum [3]. They observed a direct relation between the total dose and conversion after an induction period. Hayakawa *et al.* [13] grafted acenaphthylene on various polymeric films by UV radiation. They obtained colorless polymer from liquid-state, and yellowish polymer in the solid-state when initiated by γ -rays. This was attributed to high molecular weight of polymers obtained in liquid-state. The inhibition effect of chloranil in radiation-induced solid-state polymerization of this monomer was studied by Cser [14]. Both percent conversion and molecular weight decreased with inhibitor concentration. The insource and post homo and copolymerization of monomer by γ -rays were studied by Küçükayvuz *et al.* [7]. They observed an induction period up to a total dose of 80 kGy for insource polymerization at room temperature. The total conversion was 68% with a dose of 2.5 MGy. In post polymerization, the limiting conversion increased with temperature (being highest near the m.p. of monomer) and total radiation dose.

In this study, the structural relation between monomer and polymer will be investigated. Since, acenaphthylene monomer undergoes [15-17] an order-disorder phase transition, the role of crystal structure on polymerization mechanism should be interesting. Although the X-ray [15] and neutron diffraction [16] structural determination of acenaphthylene has been studied, there is no report on the structure and thermal properties of polymer and relation with that of the monomer.

EXPERIMENTAL

Material

The monomer (product of BDH company) was purified by crystallization several times in methanol. The melting point was 89°C. All the solvents were Merck quality and purified further by distillation before use.

Polymerization

About 0.5-1.0 g monomer were placed in Pyrex tubes and evacuated at 10^{-4} - 10^{-5} mm Hg pressure on a high vacuum system for 5-6 hours. The tubes were then sealed and placed in a ^{60}Co γ -ray source (Gamma cell model 220 of Atomic

Energy of Canada Limited Co.) with constant dose rate of $0.035 \text{ Mrad h}^{-1}$ for the desired time at room temperature. After the irradiation period, the tubes were broken and inner contents dissolved in small volume of toluene. The polymer were precipitated by pouring into excess amount of methanol. The precipitates were collected by filtration, then vacuum dried to constant weight. Percent conversions were calculated gravimetrically.

Measurements

The intrinsic viscosities of polymer samples were measured in Ubbelohde type glass viscometer at 25°C using toluene as solvent.

The IR spectra of monomer and polymers were obtained on Nicolet-510 FTIR Spectrophotometer using KBr pellets. The UV spectra were obtained on a Hewlett-Packard 8452-A, Diode Array Spectrophotometer using toluene as solvent. The X-ray powder diffractograms of monomer and polymers were taken on Huber's Guiner System 600 Diffractometer Camera on Enraf Nonius Delft FR552 generator equipped with Cu $K\alpha$ (X-ray tube (40 kV and 20 mA). The instrumental controls, data acquisition, and analysis were carried by connected PC and suitable software. The DSC spectra were obtained on a Perkin-Elmer Differential Scanning Calorimeter Type 4 with a scan rate of $5^\circ\text{C}/\text{min}$. The TG spectra of monomer and polymer were obtained on a V4.1C DuPont 2000 TGA with a heating rate of $10^\circ\text{C}/\text{min}$. in the nitrogen and/or air atmosphere.

RESULTS AND DISCUSSION

Solid-State Polymerization of Acenaphthylene

The percent conversion against time for radiation induced solid-state polymerization of acenaphthylene irradiated under vacuum at room temperature are plotted in Figure 1. The curve shows S-shaped kinetic with considerable induction period. It was about 700 hours of irradiation period at $0.035 \text{ Mrad h}^{-1}$ constant dose rate. The polymerization was slow initially, after about 1250 hours of irradiation only 9.5 % conversion was observed. The rate of polymerization was then increased (autoacceleration period) up to about 35% conversion, then slowed down again and conversion after a slow, but steady increase reached to limiting conversion of about 76% with an irradiation time of 9360 hours. The induction period shows that, the monomer molecules are not initially in favorable orientation for addition reaction. After receiving a certain amount of energy, the molecular orientation by rotation in their plane rearrange them to take position for a possible addition reaction. The

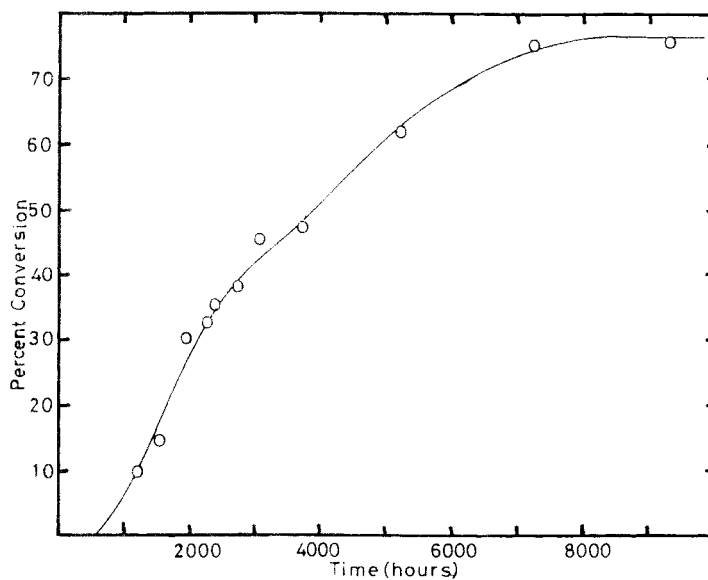


Figure 1. Conversion versus time for radiation-induced solid-state polymerization of acenaphthylene under vacuum at room temperature.

autoacceleration is a typical trend for the radical type polymerization mechanism. Some of the monomer molecules in the rearranged orientation are not in the suitable distances (van der Waals distances for vinyl group) for addition to growing chains. Therefore, they are trapped in the polymer matrix and not contributing to polymerization conversion. This is also a common observation for the radiation induced solid-state polymerization. [18]

The intrinsic viscosities and molecular weight for some of the polymer samples were measured. Some of the molecular weights with conversion given in parenthesis were as 41,300 (31.1%); 114,700 (34.3%); 71,600 (76.2%). Thus, the polymer molecular weight increases with irradiation time up to the end of autoacceleration stage, then decreases upon further irradiation at limiting conversion. This is also common for the radical type solid-state polymerization and attributed to the degradation and/or branching that takes place with irradiation of polymer.

UV and IR Spectral Investigation

The UV absorption spectrum of (a) the monomer, and (b) the polymer are shown in Figure 2. The maximum absorption wavelength λ_{\max} for the monomer is

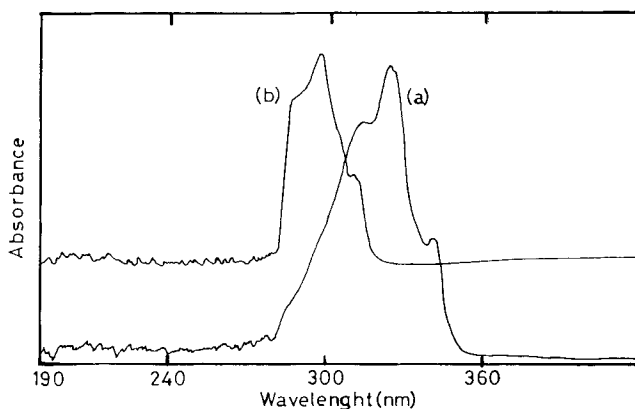


Figure 2. UV Spectrum of (a) monomer, and (b) polymer of acenaphthylene.

324 nm. Other two characteristic peaks in the form of shoulder are at 314 and 341 nm. The maximum peak in monomer spectrum shift to 297.2 nm in the UV-spectrum of polymer. The general shape of maximum peak and position of other two shoulder peaks show similarity to that of monomer peaks.

The FTIR spectrum of (a) the monomer, and (b) the polymer in region of 2000-400 cm^{-1} are given in Figure 3. The characteristic peaks for monomer in the 'fingerprint' region (1300-650 cm^{-1}) are found at 740, 790, 840, 855 and 903 cm^{-1} . The monomer peaks at 740 and 790 cm^{-1} are γ (C-H) out of plane bending and 840 cm^{-1} α (C-C-C) in plane skeletal deformation peaks. The vinyl group peaks in monomer appears at 855 and 903 cm^{-1} . The characteristic peaks in 'fingerprint' region of polymer spectrum are at 776 and 824 cm^{-1} . The disappearance of vinyl group peaks in polymer spectrum reveals the fact that the polymerization did take place through vinyl group addition as expected. In the 'group frequency' region (4000-1300 cm^{-1}) the aromatic C-H stretching are observed at around 3040 cm^{-1} in the spectra of both monomer and polymer.

According to Chen and Piirma [19], the IR spectra of amorphous poly acenaphthylene exhibits an additional band at 670 cm^{-1} which was attributed to the out-of-plane bending mode of aromatic C-H. Apparently the bending mode is physically hindered by the alignment of the polymer chain in paracrystalline state. Therefore, this band is not observed in the spectrum of our polymers which are highly crystalline. The polyacenaphthylene obtained by electroinitiation [4] and transition metal catalysts [20] showed similar characteristic absorption bands.

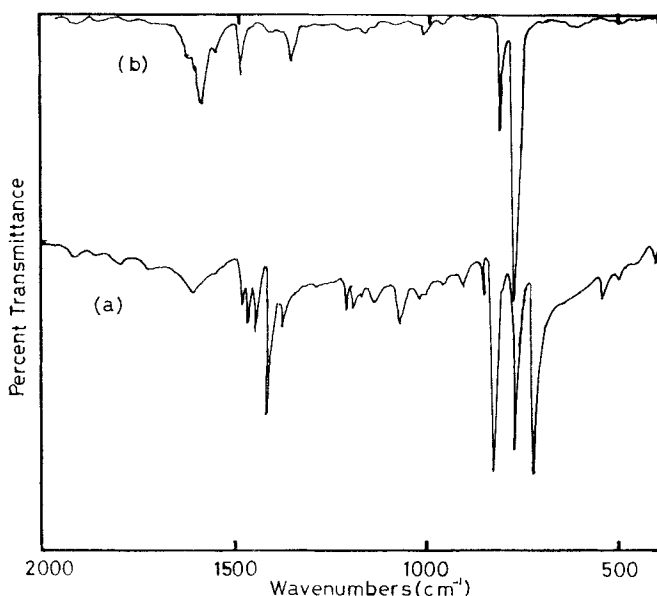


Figure 3. FTIR Spectrum of (a) monomer, and (b) polymer of acenaphthylene.

X-Ray Investigation

Acenaphthylene undergoes an order-disorder phase transition when cooled to about 130 K. This transition was explained by Sanford *et al.* [21] as a result of the rotation of molecule in its own plane. Therefore, several trials of X-ray crystal structure determination at room temperature have been unsuccessful [14, 22-23] Welberry *et al.* studied the crystal structure of this compound in detail by X-ray [15], and neutron diffraction [16] methods. Acenaphthylene crystallize in orthorhombic unit cell. The phase transition at 130 K, gives a unit cell which has c-edges doubled. The a- and b-edges remain almost the same and the number of monomer molecules, Z , increases from 4 to 8 at transition temperature. The cell parameters reported by Welberry *et al.*, are given in Table 1. The layers of closely packed molecules are stacked in the c-direction. However, there are three different molecular sites and the layers of molecules in each sites are oriented in different directions with respect to others.

In this study, the X-ray powder diffractogram of monomer and polymer were taken at room temperature (about 26°C). The monomer spectra gave 118 peaks and 90 of these could easily be indexed with chosen cell parameters. Some of the unindexed peaks that have very low intensities can be neglected. However, some

TABLE 1. Cell Parameters of Acenaphthylene Monomer and Polymers

a/pm	b/pm	c/pm	Z	Space Group	T/K	Reference
Monomer:	786.5(5)	1404.1(5)	4	Pbam or Pba2	296	11
770.5(5)	754.9(10)	2782.2(2)	8	P2 ₁ nm	130	11
758.8(13)	798.1(6)	1417.0(1)	4	P2 ₁ nm	299	This work
784.2(6)						
Polymer:						
791.2(8)	803.8(7)	1431.0(1)	4	P22 ₁ 2	299	This work

of the strong peaks could not be indexed. This must be due to a second phase in equilibrium with the main phase at room temperature. A new structure could not be solved for these peaks due to the small number of peaks. The cell parameters determined and refined in this study are also given in Table 1. There is good agreement between found values in this study and the ones given in the literature.

X-Ray powder diffractogram of polymer at different conversion percent, and the unpolymersed monomer after irradiation were also taken. The unpolymersed material was shown to be monomer, not any other impurities. The structure determined for the polymer was similar to that of monomer with small variation in cell parameters. The number of observed peaks were 110 for the polymer sample that has 45.6% conversion. About 22 of these peaks could not be indexed with chosen unit cell parameters. Thus, a second or more crystalline phase(s) is/are also exist in polymer samples also. This was observed for all polymer conversion percents. The cell parameters of different polymer samples showed very small variation and therefore, the values for polymer of 45.6% conversion is included in Table 1. The monomer and polymer structures are similar to each other. Thus, polymerization follows a topotactic mechanism. This should be expected because of layer-like structure and bulky monomer molecules.

Thermal Investigation

The DSC and TG thermograms of monomer and polymer were studied. The DSC thermogram of monomer is given in Figure 4. Thermogram shows two melting peaks at 88.3°C and 387.8°C, corresponding to the melting point of monomer and polymer, respectively. The broad peak at 217.5°C is the polymerization peak of monomer. Thus, the monomer can also be polymerized thermally

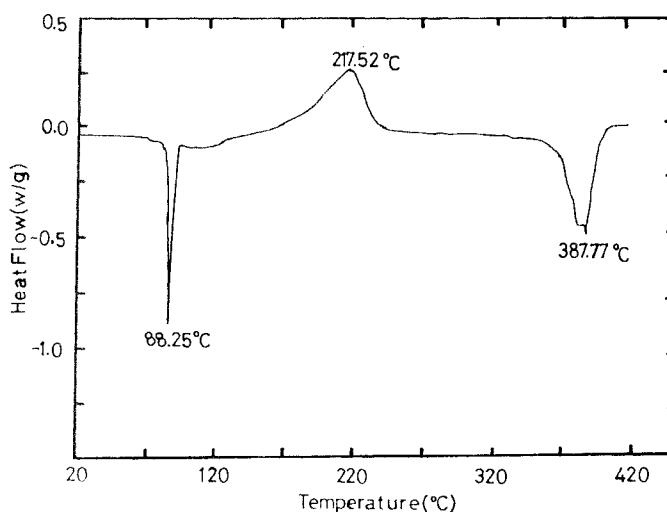


Figure 4. DSC Thermogram of acenaphthylene (heating rate = $5^{\circ}\text{C}/\text{min.}$; —: N_2 atmosphere; ---- Air atmosphere).

at this temperature. The melting peak of the monomer is quite sharp but has a small shoulder at lower temperature. The low melting point of the monomer compared to literature value is most probably due to the second crystal phase observed in X-ray diffraction. Since, a second melting peak is not observed, the melting point of two phases are quite close and second phase is in small quantity. The melting peak of the polymer is relatively broader when compared to that of monomer. This is an expected peak for a high molecular weight sample and also the presence of multi-phase components in polymer samples observed in X-ray diffraction investigation.

In order to verify the thermal polymerization of monomer further, a sample of the monomer under vacuum was kept overnight in an oven at 220°C . Then, the polymer was separated from the unpolymerized monomer as described in the experimental section and the thermogram of this polymer was taken. The thermogram of the polymer obtained by radiation (45.6% conversion) and by thermal polymerization are given in Figures 5 and 6, respectively. The T_g of the polymers are found to be 283°C and 245°C for γ -rays induced and thermal polymerized polyacenaphthylene, respectively. The T_g reported in the literature are in the range of 285 - 260°C . The high glass transition temperature is an expected consequence of greatly hindered bond rotation [3]. The effects of the chain repeat units on T_g are closely related to different factors such intermolecular forces

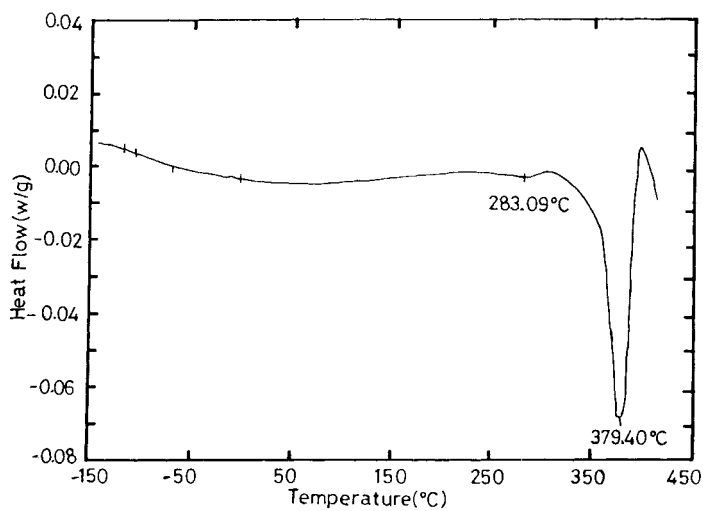


Figure 5. DSC Thermogram of polyacenaphthylene obtained by radiation polymerization (heatin rate = 5°C/min).

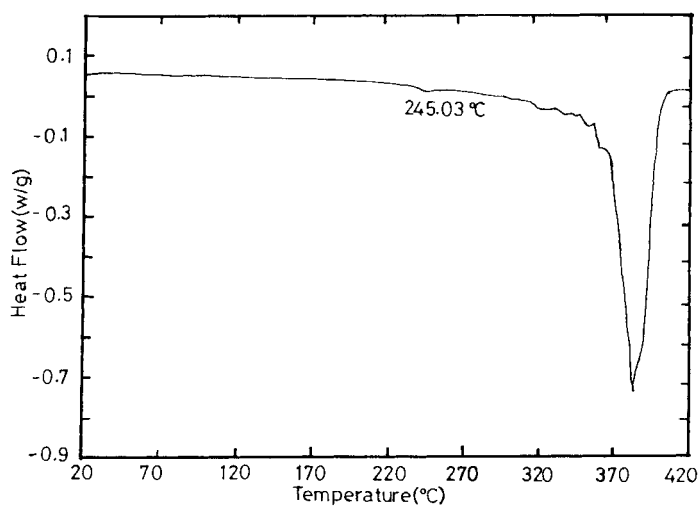


Figure 6. DSC Thermogram of polyacenaphthylene obtained by thermal polymerization (heating rate = 5°C/min).

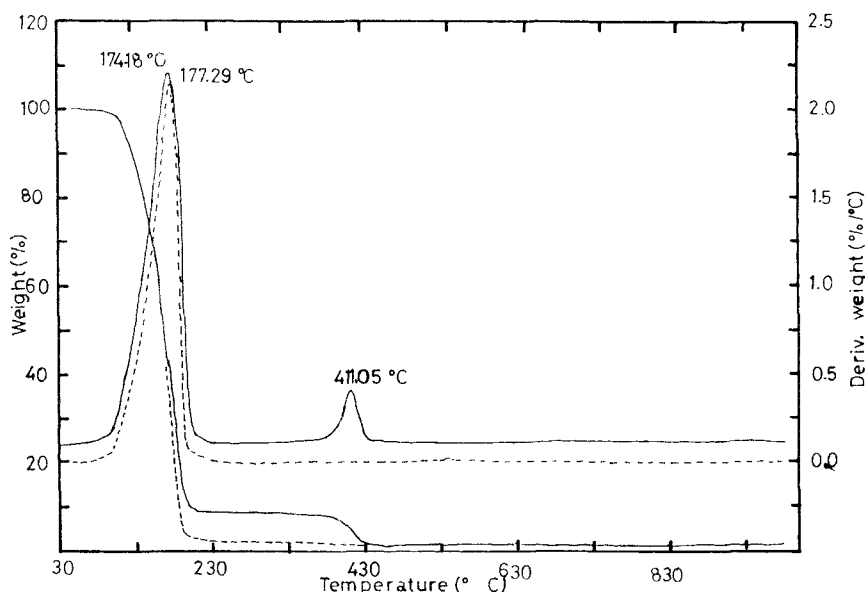


Figure 7. TG Thermogram of acenaphthylene (heating rate = 10°C/min).

including hydrogen bonding, chain stiffness, and chain symmetries. In poly-acenaphthylene the expected intermolecular forces are just van der Waals type, but the bulky aromatic group restricts segmental motion, and enhances the T_g value of the polymer. Secondary glass transition temperature for radiation induced polymer is observed at -105.4°C . This is a typical T_g behavior exhibited by polymer samples at low temperatures, i.e. between -118°C and -68°C . The melting point of polymer samples obtained by radiation and thermal polymerization are 379.4°C and 383.8°C , respectively. The melting peaks for polymers are relatively sharp, but give shoulder or split into two peaks. This is most probably due to the presence of different crystalline phases (heterogeneous structure) in polymer samples as observed in X-ray structural data. The smaller melting point (383.8°C) for thermally polymerized sample compared to the melting point (387.8°C) of polymer observed from DSC thermogram of monomer is most probably due to more heterogenous nature of the first one as can be seen on thermogram in the form of small peaks close to melting peak in Figure 6.

The TG, thermograms of monomer and polymer obtained at N_2 atmosphere are given in Figures 7 and 8, respectively. The monomer show two stage decomposition at 174.2°C and 411.1°C . The first decomposition is normal decomposition of

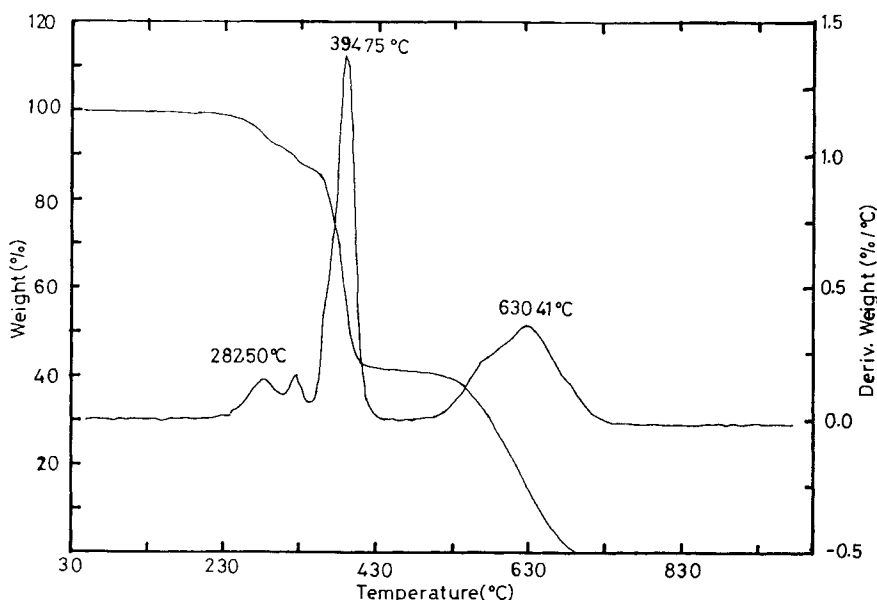


Figure 8. TG thermogram of polyacenaphthylene (heating rate = $10^{\circ}\text{C}/\text{min}$).

monomer, but some of the monomer is also polymerized in this period. The second decomposition peak corresponds to the decomposition of this polymer. When the thermogram is taken at air atmosphere (broken lines in Figure 7) due to the inhibiting effect of oxygen the polymerization does not take place and second decomposition peak is not observed. This was further tested by carrying out the thermal polymerization in the presence of air for short heating period where no polymer could be obtained.

The thermogram of polymer (45.6% conversion) in Figure 8 shows several decomposition steps at 282.5°C , 300.0°C , 394.8°C , and 630.3°C . This shows that thermal decomposition of polyacenaphthylene does not take place by a depolymerization mechanism, but by a more complicated mechanism [24]. The small decomposition peaks at temperatures ($282\text{--}300^{\circ}\text{C}$) lower than the melting point are most probably due to low molecular weight fractions of polymer.

CONCLUSION

Acenaphthylene readily polymerized by radiation in solid state giving crystalline, high molecular weight polymer. There is a correlation between crystal

structure of monomer and polymer that is an indication of topotactic polymerization mechanism under the given conditions. The polymerization methods reported up to this time gives mostly amorphous or less crystalline polyacenaphthylene. The limiting conversion of monomer to polymer is 76.2 % due to the mode of molecular packing of monomer. The high glass transition temperature is observed for polymer and decomposition temperature of polymer is quite close to its melting temperature.

REFERENCES

- [1] G. Ayrey and J. C. Bevington, *J. Macromol. Sci.-Chem.*, *A22*, 229, (1985).
- [2] P. Giusti, P. Cerrai, F. Andruzzi, and P. L. Magagnini, *Eur. Polym. J.*, *7*, 161, (1971).
- [3] J. Moacanin, A. Rembaum, R. K. Laudenslager, and R. G. Adler, *J. Macromol. Sci.-Chem.*, *1(8)*, 1497, (1967).
- [4] J. Moacanin and A. Rembaum, *J. Polym. Sci., Pt. B*, *2(10)*, 979, (1964).
- [5] E. B. Mano and B. A. L. Calafate, *J. Polym. Sci.-Polym. Chem. Ed.*, *19*, 3325, (1981).
- [6] Y. Kikuchi and H. Mitoguchi, (a) *Makromol. Chem.*, *173*, 233, (1973); (b) *J. Macromol. Sci.-Chem.*, *8(3)*, 573, (1974).
- [7] S. Küçükyavuz, Y. Ülkem, and C. Göksel, *Polym. International*, *29*, 37, (1992).
- [8] S. Küçükyavuz, C. Göhsel, and Z. Küçükyavuz, *J. Macromol. Sci.- Pure and Appl. Chem.*, *A30 (12)*, 907, (1993).
- [9] T. Oksu, M. S. Akikazu, and N. Kesiku, *J. Appl. Polym. Sci.*, *45(11)*, 1889, (1992)
- [10] R. Kulkarni, D. McIntyre, and P. Rinaldi, *Polym. Prepr.*, *32*, 128, (1991).
- [11] R. V. Kulkarni, *Diss. Abstr. Int. B*, *52*, 274, (1991).
- [12] J. Ballesteros, G. J. Howard, and L. Teasdale, *J. Macromol. Sci.-Chem.*, *A11*, 29, (1977).
- [13] K. Hayakawa, K. Kawase, and H. Yamakita, *J. Polym. Sci., Part A-1*, *10*, 2463, (1972).
- [14] F. Cser, *Acta. Chim. Acad. Sci. Hung.*, *80(3)*, 317, (1974).
- [15] T. R. Welberry, *Proc. R. Soc., London*, *334A*, 19, (1973).
- [16] R. A. Wood, T. R. Welberry, and A. D. Rae, *J. Chem. Soc. Trans.*, *11*, 451, (1985).
- [17] H. He and T. R. Welberry, *J. Chem. Soc. Perkin Trans.*, *2*, 11 (1988).
- [18] A. Usanmaz and O. K. Melad, *J. Polym. Sci. Part A, Polym. Chem.*, *34*, 1087, (1996).

- [19] C. Y. Chen and I. Piirma, (a) *J. Am. Chem. Soc. Div. Polym. Chem. Polym. Reprint*, 19(2), 608, (1978) ; (b) *J. Polym. Sci.-Polym. Chem. Ed.*, 18, 1979, (1980).
- [20] H. N. Cho and S. K. Choi, *J. Polym. Sci., Part A, Polym. Chem. Ed.*, 25, 15, (1987).
- [21] W. E. Sanford, G. J. Kupferschmidt, C. A. Fyfe, R. K. Boyd, and J. A. Ripmeester, *Can. J. Chem.*, 58, 906, (1980).
- [22] M. D. Cohen, I. Ron, G. M. Schmidt, and J. M. Thomas, *Nature*, 224, 167, (1969).
- [23] R. Gordon and R. F. Yang, *J. Mol. Spectrosc.*, 34, 266, (1970).
- [24] A. Flores, A. Laringanana, J. Goikuria, M. Rodriguez, and L.M. Leon, *Thermochin Acta* , 221(1) , 123, (1993).

Received November 1, 1996

Final revision received September 10, 1997