

SYNTHESIS AND CHARACTERIZATION OF POLYMETHACRYLATES BEARING HETEROCYCLIC AZO GROUP AND MESOGENIC GROUP FOR NONLINEAR OPTICS

ZHANG Huiqi (张会旗)^{1,2} LI Chenxi (李晨曦)² HUANG Wenqiang (黄文强)²

YIN Shougen (印寿根)² WU Qiang (吴强)² SONG Zhengji (宋正纪)²

and HE Binglin (何炳林)¹

¹(The State Key Laboratory of Functional Polymer Materials for Adsorption and Separation,
Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China)

²(Department of Applied Chemistry, Tianjin University, Tianjin 300072, China)

Abstract The methacrylate monomers bearing mesogenic group and heterocyclic azo dye have been synthesized. The monomeric dye was copolymerized with the mesogenic monomer using a free radical initiator to produce polymers useful for nonlinear optics. The monomers and polymers were characterized by IR, ¹H-NMR, and UV-Vis spectra. The average molecular weight ($\overline{M}_w$ and $\overline{M}_n$) of the polymers were determined by gel permeation chromatography. The thermal properties of the polymers such as thermal stability and phase transition behavior were studied by thermogravimetric analysis, differential thermal analysis, polarizing optical microscope and X-ray diffractometer. The results demonstrate that the synthesized polymers are crystalline polymers at room temperature and no liquid crystalline phases were observed for all of them.

Keywords Heterocyclic azo group; Mesogenic group; Nonlinear optics; Liquid crystalline polymers; Crystalline polymers; Polymethacrylate

INTRODUCTION

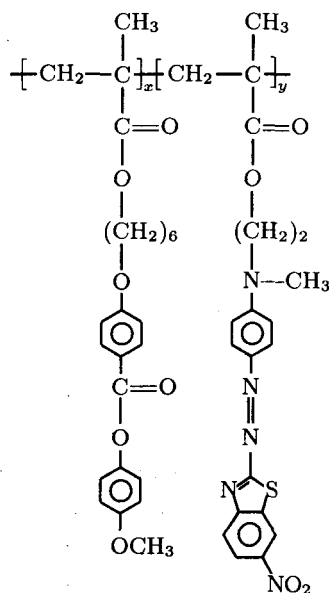
Recent advances in optical communication have created intense interest in nonlinear optical (NLO) materials^[1,2]. Although optical devices based on inorganic materials such as LiNbO₃ have already become available, much research has been directed to organic NLO materials that can possess larger susceptibilities^[3-6], higher resistance to laser, fast optical response, and simpler processing methods.

In general, organic molecules bearing electron donor and acceptor groups separated by large conjugated frameworks have been shown to possess large values of the second order molecular hyperpolarizability β ^[3-6]. A number of authors have examined the NLO properties of such molecules dispersed in glassy polymer hosts^[7-10] and in liquid crystalline polymer hosts^[11]. However, host/guest systems suffer from

limited solubility of the NLO molecule in the polymer host, and the orientation in glassy polymer matrices is gradually lost over a few days at room temperature^[10].

A more advantageous arrangement is to connect the active NLO species covalently to the polymer backbone, and a number of such polymers have been prepared^[11-14]. In this way, stable, high loading levels of NLO-active material in a polymer can be achieved. Side-chain liquid crystalline polymers have recently been recognized as the most promising candidate for NLO applications because they combine the above advantages with a potential for enhanced alignment on poling, stable alignment at room temperature, and a resultant more efficient response^[12,13,15].

This paper describes the synthesis and characterization of the copolymers containing different compositions of nonmesogenic heterocyclic azo monomer as a NLO component and mesogenic monomer which tends to orientate by application of an external field in homogeneous or in homotropic alignment depending on the dielectric anisotropy of the mesogenic group as shown in Scheme 1.



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Scheme 1

EXPERIMENTAL

Chemicals and reagents

All the reagents and solvents used are commercially available and of C.P. or A.P. grade.

Measurements

Elemental analyses were performed with a Foss Heraeus C—H—N analyser. UV-Vis spectra were recorded on a Shimadzu UV-2101 PC UV-Vis scanning spectrophotometer. Infrared spectra were obtained as a potassium bromide pellet with a Nicolet 5DX spectrophotometer. ¹H-NMR spectra were obtained with a Varian Unity-400 MHz NMR spectrometer. The number- and weight- average molecular weights ($\overline{M}_n$ and $\overline{M}_w$), and polydispersity index values of the polymers were determined with a Waters gel permeation chromatography equipped with three ultrastyrigel columns and a differential reflective index R-410 detector. The molecular weights of the polymers were calibrated against polystyrene standards using tetrahydrofuran as mobile phase. Thermogravimetric analyses and glass transition temperatures of the poly-

mers were recorded with a Rigaku Standard type TG-DTA analyser at a heating rate of 10°C/min in air. The polarizing optical microscopic (POM) observations were made with a XPR-2 type polarizing microscope equipped with a hot stage (Nanjing Instrument Factory). X-ray diffraction were performed with a BDX-3200 X-ray diffractometer (Peking University Instrument Factory) at room temperature with a scanning rate of 4°/min.

Monomer synthesis

Mesogenic monomers The methacrylate monomers with mesogenic group were prepared according to the method described by Ringsdorf et al.^[16,17]. The analytical data are shown below:

MAPB2: Yield, 88%. mp. 66~67°C

MAPB6: Yield, 82%. mp. 45~46°C

Para-nitrophenylthiourea A mixture of p-nitroaniline (92 g), concentrated hydrochloride (86 ml), and distilled water (300 ml) was stirred at room temperature for 30 min. A solution of ammonium thiocyanate (60.8 g) dissolved in water (200 ml) was added and the reaction mixture was heated to 80°C for 5 h. After cooling, the precipitated yellow product was filtered, washed thoroughly with water/ethanol mixture ($v/v = 1/1$), and the pure product was obtained. Yield, 80%, mp. 203~204°C (Lit.^[18] 206°C)

2-Amino-6-nitrobenzothiazole^[19] A mixture of concentrated sulfuric acid (80 ml), p-nitrophenylthiourea (40 g), silica (2.4 g), and ammonium bromide (1.6 g) was heated to 100~105°C with stirring for 5 h, then cooled and poured into distilled water (300 ml). The solution was heated to 95°C, and was immediately filtered. The filtrate was neutralized with concentrated ammonia to pH 3.5, heated to 70°C, and then the precipitated product was filtered and washed with warm water, a yellow product was obtained. Yield, 91%, mp. 247~249°C (decomp.)

N-(2-hydroxyethyl)-N-methylaniline^[20] A mixture of freshly distilled N,N-dimethylaniline (100 ml) and 2-chloroethanol (33 ml) was heated and refluxed with vigorous mechanical stirring for 8 h. The residue was fractionally distilled in vacuo to produce a colorless oil. Yield, 46%, bp. 148~152°C/7 mmHg.

2-{4-[N-(2-hydroxyethyl)-N-methyl] phenylazo}-(6-nitro) benzothiazole Nitrosyl sulfuric acid was prepared by mixing sodium nitrite (7.6 g) with concentrated sulfuric acid (50 g) at 0°C and slowly warming up to stirred mixture to 70°C until homogeneous. The nitrosyl sulfuric acid was added to a chilled mixture of glacial acetic acid (350 g) and propionic acid (50 g). To this solution was added 2-amino-6-nitrobenzothiazole (19.5 g). The solution was stirred at 10°C for 2 h. This diazonium mixture was added to a stirred mixture of N-(2-hydroxyethyl)-N-methylaniline (16.6 g), methanol (300 g), ice water (300 g), and crushed ice (100 g). After stirring for 1 h at room temperature, the precipitated product was filtered, washed with wa-

ter and dried in vacuum at 100°C to give pure product. Yield, 40%, mp. 223°C. IR (KBr, cm^{-1}): 3400 ($-\text{OH}$), 1604.4, 1544.9 (aromatic, $\text{C}=\text{C}$), 1441.7 ($\text{N}=\text{N}$), 1302.5 ($-\text{NO}_2$); ^1H -NMR ($\text{SO}(\text{CD}_3)_2$, TMS) δ = 8.97–7.00 (m, 7H, Ar-H), 3.68 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{N}-$), 3.21 (s, 3H, $-\text{CH}_3$).

2- { 4- [N-(2- methacryloylethyl) -N-methyl] phenylazo }-(6-nitro) benzothiazole (MAHAZO) To a stirred mixture of 2-{4-[N-(2-hydroxyethyl)-N-methyl]phenylazo}-(6-nitro) benzothiazole (1.8 g), dry, distilled tetrahydrofuran (60 ml), and triethylamine (2 ml) at 0°C was added dropwise methylacryloylchloride (2 ml). The reaction mixture was stirred at 0°C for 2 h and then at 25°C for 24 h. The reaction was stopped and the mixture was poured into water. The precipitated product was filtered and washed with distilled water to give a dark red product. Yield, 90%, mp. 153°C. IR (KBr, cm^{-1}): 1711.3 ($-\text{COO}-$), 1640 ($\text{H}_2\text{C}=\text{C}-$), 1599.6, 1518.9 (aromatic, $\text{C}=\text{C}$), 1455.6 ($\text{N}=\text{N}$), 1309.0 ($-\text{NO}_2$); ^1H -NMR (CDCl_3 , TMS) δ =8.74–6.84 (m, 7H, Ar-H), 6.06 and 5.58 (2s, 2H, $\text{CH}_2=\text{C}-$), 4.41–3.85 (m, 4H, $-\text{NCH}_2\text{CH}_2\text{O}-$), 3.22 (s, 3H, $-\text{NCH}_3$), 1.89 (s, 3H, $=\text{C}-\text{CH}_3$), 7.248 and 1.626 (CDCl_3). UV-Vis (CHCl_3): λ_{max} =527 nm.

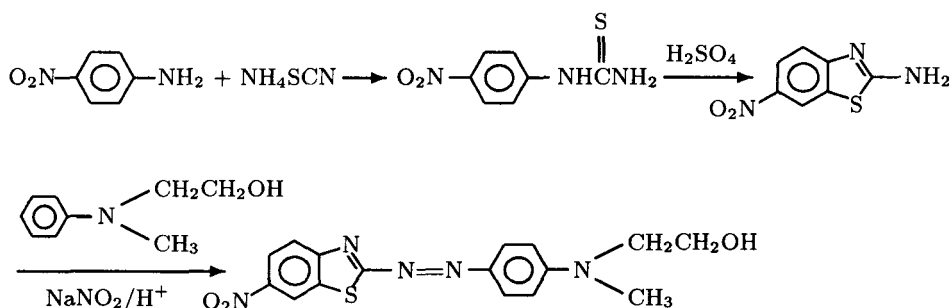
Polymer synthesis

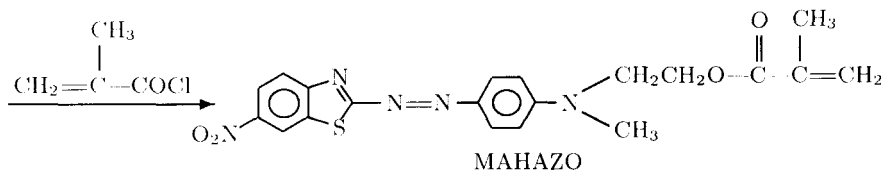
The polymerization was carried out in tetrahydrofuran (THF) or N,N-dimethylformamide (DMF) with 2% by mole 2, 2'-azobis(isobutyronitrile) (AIBN) as initiator. The mesogenic monomer MAPB6 and azo monomer MAHAZO were allowed to polymerize in different mole ratio under nitrogen at 67°C for 2 days. The polymerization was stopped by pouring the reaction mixture into ethanol (or methanol). The obtained polymers were washed with warm ethanol and finally dried at 60°C under vacuum for 2 days.

RESULTS AND DISCUSSION

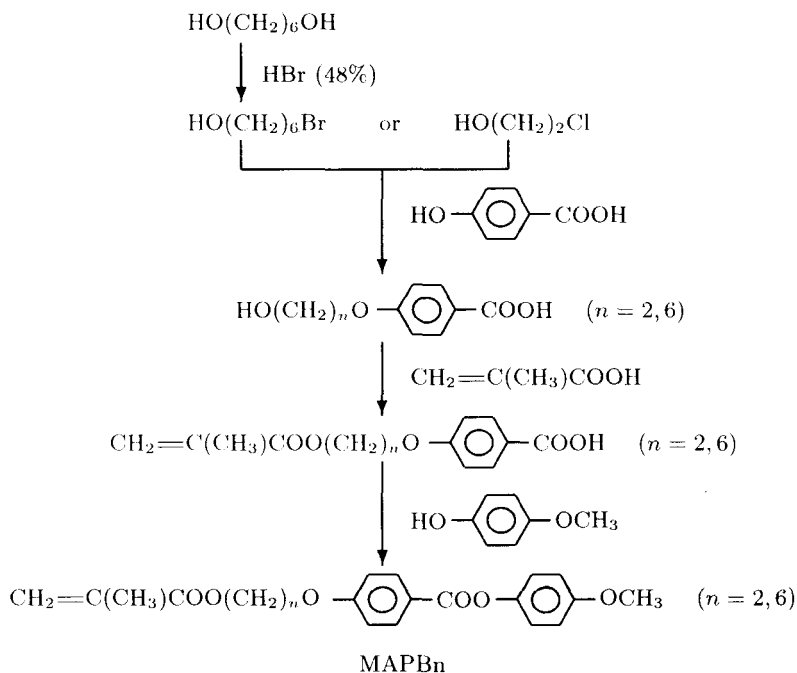
Synthesis

The methacrylate azo monomer and methacrylate mesogenic monomers were prepared as illustrated in Scheme 2 and 3, respectively.





Scheme 2



Scheme 3

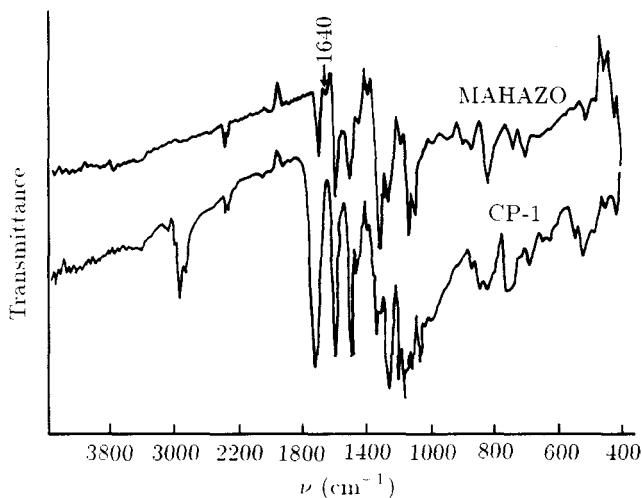


Fig. 1 Infrared spectra of MAHAZO and CP-1

All monomeric methacrylates were obtained with satisfying purity and in good

yield, and the structure of the new heterocyclic azo monomer was identified by IR (Fig. 1), UV-Vis (Fig. 2), and ^1H -NMR spectra (Fig. 3a).

The monomeric azo dye did not exhibit liquid crystalline behavior when examined by polarizing optical microscopy.

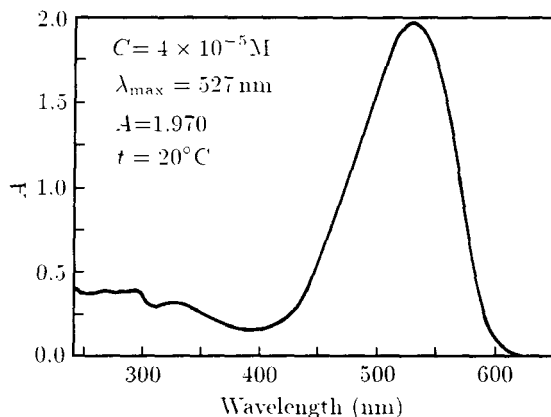


Fig. 2 UV-Vis spectrum of MAHAZO in chloroform

The free radical polymerization of the monomeric dye with the mesogenic monomer in different compositions was carried out in THF or DMF solvent at 67°C using AIBN as initiator to form copolymers. The polymerization data and characteristics of the polymers are given in Table 1. The completeness of the polymerization was established by disappearance of the vinyl proton signals of the methacrylic group at 5.58 and 6.06 ppm in the ^1H -NMR spectrum (Fig. 3b) and of the vinyl absorption at 1640 cm^{-1} in the IR spectrum (Fig. 1).

Table 1 Polymerization data and characteristics of the polymers

Polymer	Solvent	Yield (%)	$m_{\text{feed}}^{\text{a)}$	$m_{\text{polymer}}^{\text{b)}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
CP-1	THF	60.6	0.05	0.23	20.5	15.7	1.31
CP-2	DMF	22.7	0.10	0.31	24.7	18.8	1.32
CP-3	THF	38.1	0.15	0.35	14.5	13.0	1.12
CP-4	DMF	5.6	0.20	0.50	19.4	15.6	1.24

a) Mole fraction of the azo monomer in all the added monomers.

b) Mole fraction of azo unit in polymer determined by elemental analysis.

The compositions of the copolymers were estimated by elemental analyses. The results showed that great difference appeared between the initial monomer ratio and the copolymer composition, indicating that the reactivity of the azo monomer is higher than that of the mesogenic monomer. It also shows that DMF has a bigger retarding effect on the radical polymerization than THF.

The weight and number average molecular weights, $(\overline{M}_w)$ and $(\overline{M}_n)$ and polydispersity index $(\overline{M}_w/\overline{M}_n)$ values of the polymers were determined by gel permeation

chromatography. The results reveal that $\overline{M}_n$ ranges from 13000 to 18800, and the $\overline{M}_w/\overline{M}_n$ values of the polymers are in the range of 1.21 ~ 1.31.

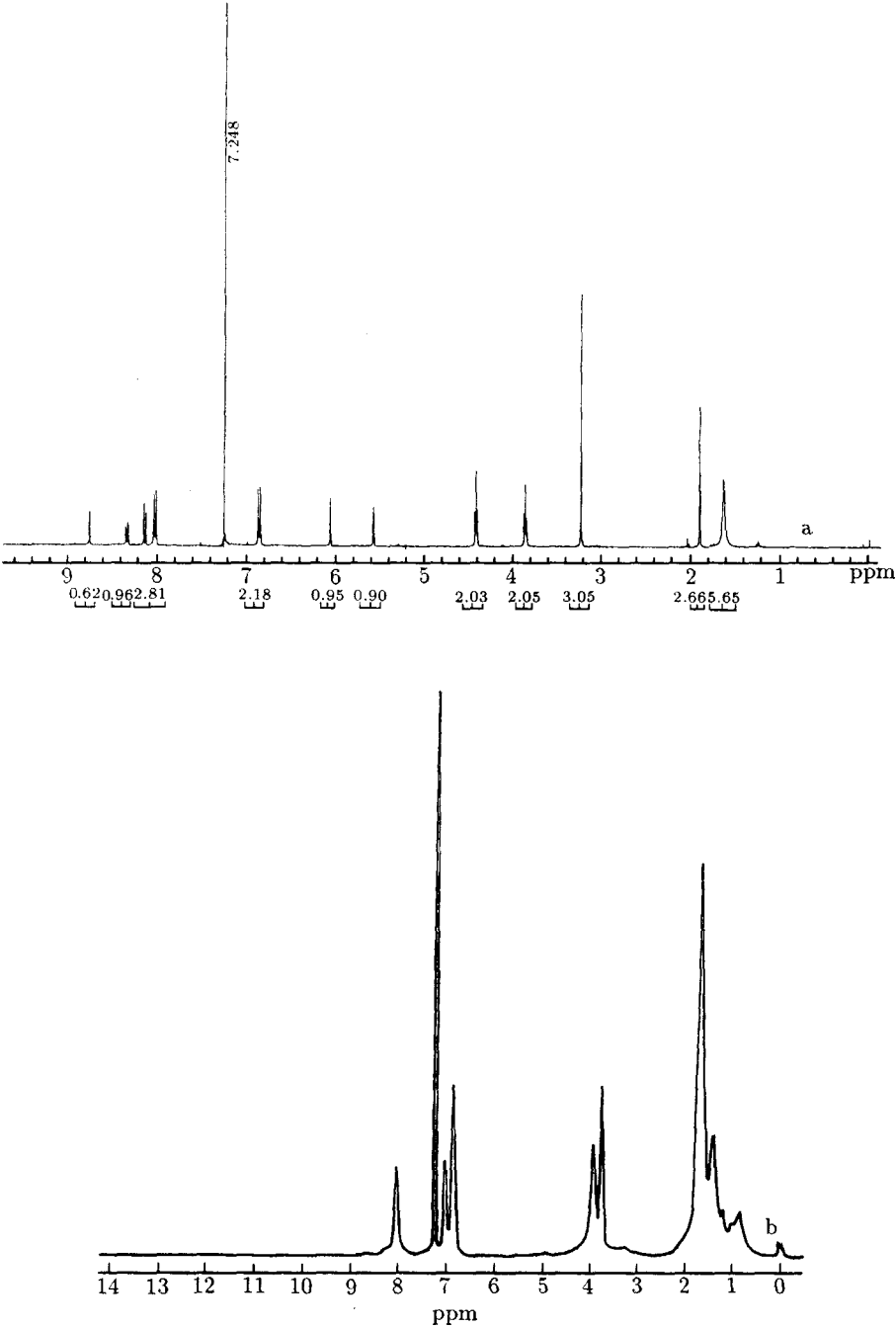


Fig. 3 ¹H-NMR spectra of MAHAZO (a) and CP-1 (b) in CDCl₃

Thermal behavior

The thermal stability of the polymers was studied by thermogravimetric analysis in air. The TGA traces of the polymers are shown in Fig. 4. The results show that the initial decomposition temperatures of all the polymers are above 240°C, indicating that they have very good thermal and thermal oxidative stability.

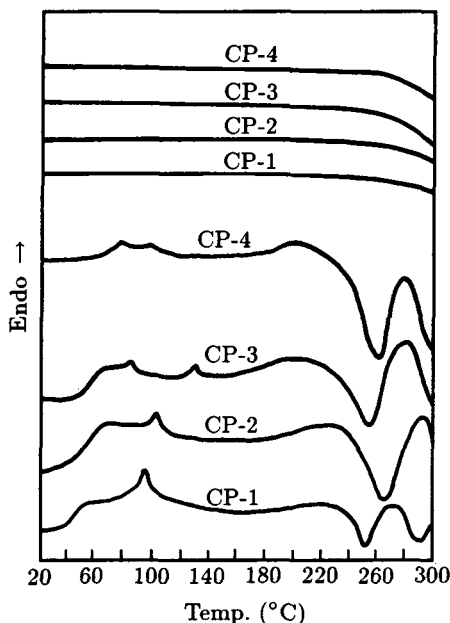


Fig. 4 TGA and DTA diagram of the polymers with increasing temperature at a rate of 10°C/min

The phase transition behavior of the polymers, investigated by DTA, is also presented in Fig. 4. It can be seen that in addition to the glass transition at 47~73°C, characteristic of polymethacrylate backbone, all the copolymers have one to two endotherms before decomposition.

The assignment of the endotherms was conducted by POM observation and X-ray diffraction measurement.

POM investigations were carried out on thin polymer films between two slides. The polymer films were subjected to different thermal treatment with the primary aim of promoting the formation and identification of optical textures typical of liquid crystal phases. However, it was impossible to observe any specific liquid crystal textures for all of the copolymers, while the homopolymer of the mesogenic monomer MAPB6 was reported to show a nematic liquid crystalline phase between 46°C and 111°C^[16]. It has been well established that the copolymerization of a certain amount of nonmesogenic monomers with mesogenic monomers can suppress the liquid crystallinity of the obtained polymers, which is commonly observed for both

side-chain and main chain liquid crystalline polymers^[21-24]. The results of the POM observations indicate that the copolymerization of 23 mol% of the heterocyclic azo monomer MAHAZO with the mesogenic monomer MAPB6 can completely suppress the formation of the liquid crystalline phase of the obtained polymers. Accordingly, the endotherms can only be assigned to crystal-melting peaks. It is worthwhile noting that the copolymer CP-3 has double melting peaks.

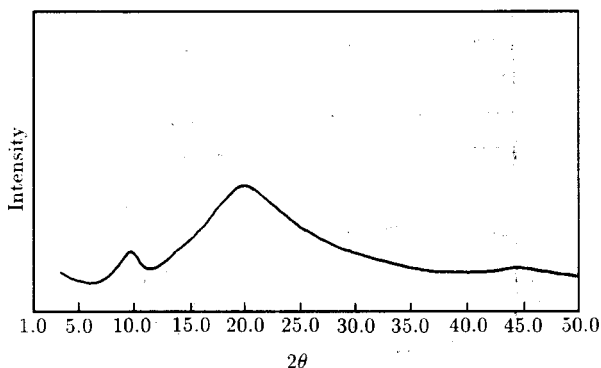


Fig. 5 X-ray diffractogram of the unoriented copolymer CP-3 at room temperature

Fig. 5 shows the X-ray diffractogram of the unoriented copolymer CP-3 with an azo content of 35 mol-% at room temperature, which is a representative of the X-ray diffractograms of the other copolymers. It displays that the crystallinity of the polymer is rather low.

REFERENCES

- [1] Williams, D.J., Ed., "Nonlinear Optical Properties of Organic and Polymeric Materials", ACS Symposium Series 233, American Chemical Society, Washington, D. C., **1983**
- [2] Chemla, D.S., Zyss, J., "Nonlinear Optical Properties of Organic Molecules and Crystals", Academic Press, New York, **1987**
- [3] Williams, D.J., *Angew. Chem. Int. Engl.*, **1984**, *23*, 690
- [4] Katz, H.E., Singer, K.D., Sohn, J.E., Dirk, C.W., King, L.A., Gordon, H.M., *J. Am. Chem. Soc.*, **1987**, *109*, 6561
- [5] Buckley, A., Choe, E.W., Demartino, R.N., Leslie, T.M., Nelson, G., Stamatoff, J.B., Stuetz, D.E., Yoon, H.-N., *Polym. Mat. Sci. Eng.*, **1986**, *54*, 502
- [6] Ulman, A., *J. Phys. Chem.*, **1988**, *92*, 2385
- [7] Meredith, G.R., Vandusen, J.G., Williams, D.J., *Macromolecules*, **1982**, *15*, 1385
- [8] Singer, K.D., Sohn, J.E., Lalama, S.J., *Appl. Phys. Lett.*, **1986**, *49*, 248
- [9] Demartino, R.N., *U.S. Pat.*, *4*, 717, 508, **1987**
- [10] Hampsch, H.L., Yang, J., Wong, G.K., Torkelson, J.M., *Macromolecules*, **1988**, *21*, 526
- [11] Lebarney, P., Ravaux, J.C., Parneix, J.P., Njeumo, R., Legrand, C., Levelut, A.M., *Proc. SPIE*, **1987**, *682*, 56

- [12] Griffin, A.C., Bhatti, A.M., Hung, R.S.L., *Proc. SPIE*, **1987**, 682, 65
- [13] Matsumoto, S., Kubodera, K., Kurihara, T., Kaino, T., *Appl. Phys. Lett.*, **1987**, 51 (1), 1
- [14] Demartino, R.N., Yoon, H.-N., Stamatoff, J.B., Buckley, A., *U.S. Pat.*, 4,694,066, **1987**
- [15] Leslie, T.M., Demartino, R.N., Choe, E.W., Khanarian, G., Haas, D., Nelson, G., Stamatoff, J.B., Stuetz, D.E., Teng, C.-C., Yoon, H.-N., *Mol. Cryst. Liq. Cryst.*, **1987**, 153, 451
- [16] Portugall, M., Ringsdorf, H., Zentel, R., *Makromol. Chem.*, **1982**, 183, 2311
- [17] Happ, M., Ringsdorf, H., Finkelmann, H., *DE. Pat.*, 27 22 589 A1, **1978**
- [18] Aldrich, **1992—1993**, 19,937-0
- [19] Rentel, H., Papenfuhs, T., *E.P. Pat.*, 0, 207, 416 A1, **1987**
- [20] Nokuti, S., Yu, B., *Nihon Kagaku Zasshi*, **1952**, 73, 331
- [21] Huang, Z.H., Yang, C.C., Tang, X.Y., Wang, H.B., Jing, X.B., *Chem. J. Chinese Univ.*, **1994**, 15 (1), 136
- [22] Robello, D.R., *J. Polym. Sci., Part A: Polym. Chem.*, **1990**, 28 (1), 1
- [23] Zhang, Q.Z., Wang, Y., Hou, J.A., Xu, M., *Chem. J. Chinese Univ.*, **1994**, 15 (10), 1563
- [24] Lenz, R.W., Jin, J.-I., *Macromolecules*, **1981**, 14, 1405