

SYNTHESIS AND CHARACTERIZATION OF COMB-LIKE POLYMERS BEARING HETEROCYCLIC AZO GROUP AND MESOGENIC GROUP

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Abstract The synthesis and characterization of a series of novel comb-like polymethacrylates bearing heterocyclic azo group and mesogenic group are described. The thermal properties of the polymers such as thermal stability and phase transition behavior were investigated by thermogravimetric analysis, differential thermal analysis and polarizing optical microscopy techniques. The experimental results show that all the synthesized polymers do not exhibit liquid crystallinity except the homopolymer of the mesogenic monomer MAPB2 and the glass transition temperatures of the polymers increase with increasing content of azo moiety in polymers linearly.

Keywords Comb-like polymers, Heterocyclic azo group, Mesogenic group

INTRODUCTION

Recently much interest has been directed to the behavior of photoresponsive comb-like polymers with polyphosphazene^[1], polyurethane^[2], polypeptide^[3,4], polymethacrylate^[5,6] or polymethacrylamide^[6-8] backbones and azo groups in the side chains due to their potential use in electro-optical and reversible optical information storage devices^[9-12]. Until now, a lot of comb-like polymers containing various azo groups in the side chains have been synthesized and studied, but few comb-like polymers containing heterocyclic azo groups have been investigated. Thus the present paper deals with the synthesis and characterization of a series of new comb-like polymers bearing the benzothiazole heterocyclic azo group and the mesogenic group in the side chain attached via a flexible alkyl spacer as shown in Scheme 1.

EXPERIMENTAL

Materials

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

Measurements

The proton spectra were obtained with a Varian Unity plus 400 NMR spectrometer. Infrared spectra were obtained as a potassium bromide pellet with a Nicolet 5DX spectrophotometer. UV-Vis spectra were recorded on a Shimadzu UV-2101 PC UV-Vis scanning spectrophotometer. Elemental analyses were performed with a Foss Heraeus C-H-N analyser. The number and weight

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3.16 (s, 3H, —NCH₃—); UV-Vis (THF) $\lambda_{\max}$ = 502.5 nm.

2-[4-(N-methacryloyl-ethyl-N-methyl) phenylazo]benzothiazole (HAZO): A mixture of 2-[4-(N-2-hydroxyethyl-N-methyl)phenylazo]benzothiazole (3.12 g, 0.01 mol), dry THF (160 mL) and distilled triethylamine (2.8 mL) was cooled to 0 °C and treated dropwise with freshly distilled methacryloyl chloride (9 mL). The reaction mixture was stirred at 0 °C for 1 h and then at 25 °C for 24 h. The insoluble part was filtered off and water was added to the filtrate to precipitate the product. The precipitated product obtained was filtered, washed with water and the crude product was purified by column chromatography on silica gel with chloroform/methanol = 15/1 (v/v) as the solvent. Yield: 85%, m.p. 142 °C (DSC); IR (KBr, cm⁻¹) ν = 1713.5 (—C=O), 1636.0 (CH₂=C—), 1601.6, 1521.8 (aromatic, C=C), 1551.9 (C—N), 1449.2 (N=N); ¹H-NMR (SO(CD₃)₂) δ = 8.04~7.00 (*m*, 8H, Ar-H), 5.97 and 5.65 (2*s*, 2H, CH₂=C—), 4.34~3.89(*m*, 4H, —OCH₂CH₂N—), 3.15 (*s*, 3H, —NCH₃), 1.80 (*s*, 3H, —CH₃); UV-Vis (CHCl₃) $\lambda_{\max}$ = 491 nm.

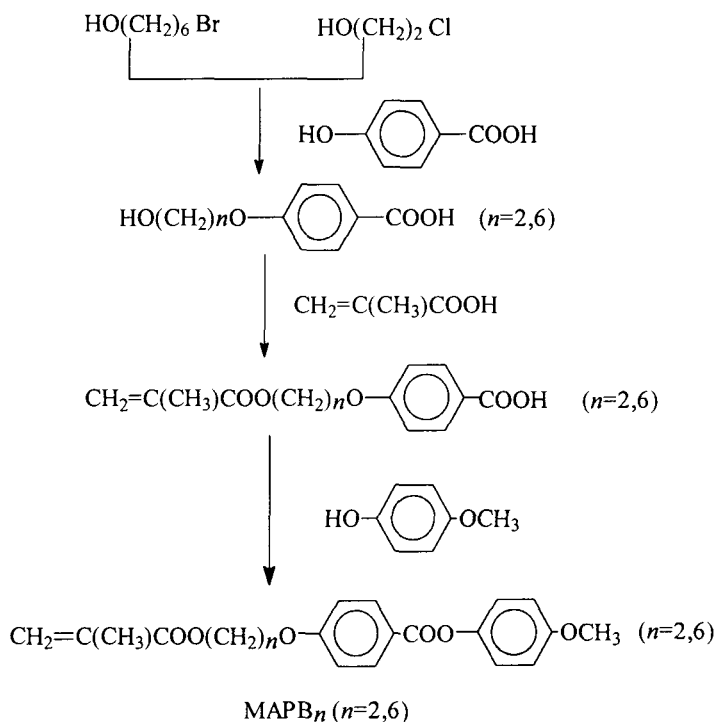
Polymer Synthesis

All homo- and copolymers were synthesized by free radical polymerization according to the following general procedure: The monomer or monomer mixture (1 g) was dissolved in dry THF (10 mL). To the monomer solution was added 2, 2'-azobis(isobutyronitrile) (AIBN) (2 mol% of monomer or monomer mixture). The reaction mixture was refluxed under nitrogen for 48 h. The resulting solution was cooled and poured into ethanol to precipitate the polymer. The polymers so obtained were purified by washing with warm ethanol and then dried in vacuo at 80 °C for 48 h.

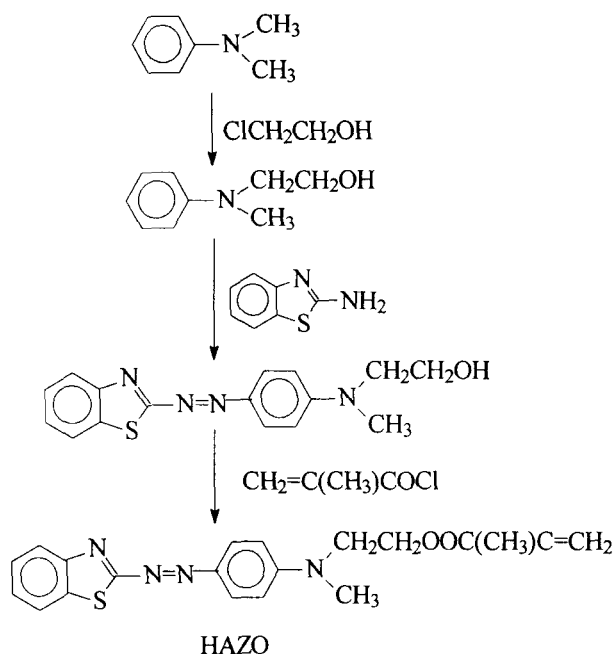
RESULTS AND DISCUSSION

Synthesis

The synthesis of the methacrylate mesogenic monomers and methacrylate azo monomer is presented in Schemes 2 and 3.



Scheme 2



Scheme 3

All monomeric methacrylates were obtained with satisfactory purity and in good yield, and the new heterocyclic azo monomer was characterized with $^1\text{H-NMR}$, IR and UV-Vis spectroscopy.

The methacrylate azo monomer and the methacrylate mesogenic monomers exhibit only defined melting points and no liquid crystalline behavior could be detected.

The polymerization of the monomers or the monomer mixtures was carried out using AIBN as the initiator and THF as the solvent at 67°C . All the polymers were purified by washing with warm ethanol until no monomers could be detected. An acceptable yield could be reached (Table 1). The completeness of the polymerization was further established by the disappearance of the vinyl proton signals of the methacrylic group at 5.97 and 5.65 in the $^1\text{H-NMR}$ spectrum (Fig.1) and of the vinyl absorption at 1636 cm^{-1} in the IR spectra (Fig.2).

Table 1. Polymerization data and characteristics of the polymers

Polymer	n	m_{feed}^1	Yield (%)	$M_n^2 \times 10^{-4}$	$M_w^2 \times 10^{-4}$	M_w/M_n
Poly-1	2	0.00	93.0	2.48	4.26	1.72
Poly-2a	2	0.25	91.8	1.78	2.49	1.40
Poly-2b	2	0.50	63.5	1.93	2.75	1.42
Poly-2c	2	0.75	76.2	1.59	2.05	1.29
Poly-6a	6	0.25	16.0	1.67	2.26	1.35
Poly-6b	6	0.50	37.3	1.62	2.10	1.30
Poly-6c	6	0.75	50.6	1.65	2.19	1.33
Poly-2	—	1.00	28.0	1.41	1.74	1.23

1. Mole fraction of azo monomer in all the added monomers;

2. Determined by GPC, polystyrene standards, THF mobile phase

The molecular weights of all the polymers and their molecular weight distribution were obtained from gel permeation chromatography, and the results are summarized in Table 1. It can be seen that the polymers have number-average weights (M_n) from about 14100 to 24800 and polydispersity index (M_w/M_n) from about 1.23 to 1.72.

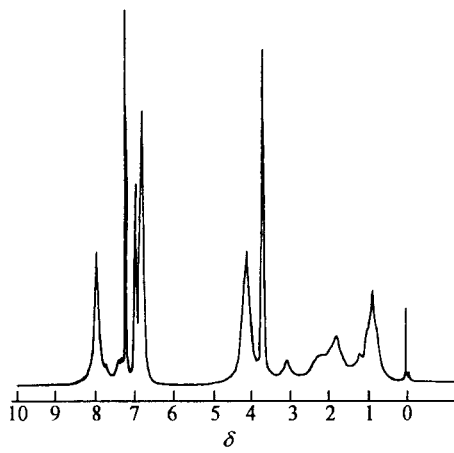


Fig.1 ¹H-NMR spectrum of poly-2a (CDCl₃)

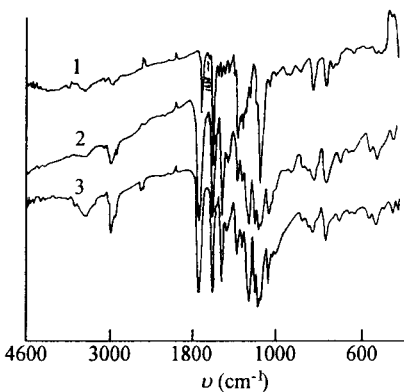


Fig.2 IR spectra of HAZO, poly-2a and poly-6a
1. HAZO, 2. Poly-2a, 3. Poly-6a

The composition of the polymers was determined with elemental analysis and the results are listed in Table 2. The results show that there exists good agreement between the initial comonomer ratio and the copolymer composition, indicating that the azo monomer has similar reactive activity with the mesogenic monomers.

Table 2. Elemental analysis and glass transition temperatures of the polymers

Polymer	<i>n</i>	Elemental analysis (%)			<i>m</i> _{polymer} ¹	<i>w</i> _{polymer} ²	<i>T_g</i> (°C)
		C	H	N			
Poly-1	2				0.00	0.0	87
Poly-2a	2	65.8	5.8	3.0	0.20	21.3	108
Poly-2b	2	64.6	5.7	7.2	0.51	52.9	127
Poly-2c	2	63.7	5.6	10.6	0.81	81.5	152
Poly-6a	6	61.3	6.1	3.4	0.24	22.8	83
Poly-6b	6	65.8	5.7	6.5	0.46	44.1	102
Poly-6c	6	64.6	5.1	11.2	0.78	76.3	147
Poly-2	—				1.00	100	170

1. Mole fraction of the azo unit in polymers determined by elemental analysis;

2. Weight percentage of the azo unit in polymers determined by elemental analysis

Thermal Behavior

The thermal stability of the obtained polymers was studied by thermogravimetric analysis (TGA) in air. The TGA traces of the polymers are shown in Fig.3. It can be seen that the initial decomposition temperatures of all the polymers are above 240°C, which indicates that they have good thermal stability.

Figure 3 also shows the typical DTA thermogram of polymers on the heating mode. It can be seen that in addition to glass transition (Table 2), all the polymers have one endotherm before decomposition except Poly-2.

In order to assign the endotherms, the polymer films were subjected to differential thermal treatment with the primary aim of enhancing the optical textures typical of liquid crystalline phases. However, it was impossible to observe any specific liquid crystalline textures for all of the synthesized polymers containing azo group, while poly-1, the homopolymer of the mesogenic monomer MAPB2, clearly shows the nematic liquid crystalline phase, as observed previously^[13]. 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^[16-19]. The POM investigations indicate that the copolymerization of 20 mol% of HAZO with MAPB2 and 24 mol% of HAZO with MAPB6 can completely suppress the formation of the liquid crystallinity of the obtained polymers. Therefore, the endotherm of poly-1 is assigned to the phase transition from nematic phase to isotropic phase, while no specific assignment is determined for the endotherms of the copolymers, which might be due to the thermal fragmentation of the polymers.

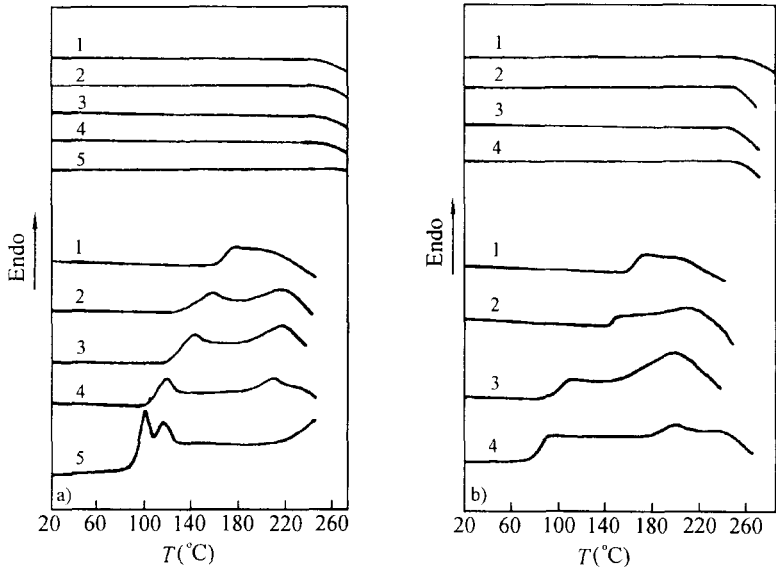


Fig. 3 TGA and DTA curves of the polymers with increasing temperature at a rate of 10°C/min
a) 1. Poly-2, 2. Poly-2c, 3. Poly-2b, 4. Poly-2a, 5. Poly-1,
b) 1. Poly-2, 2. Poly-6c, 3. Poly-6b, 4. Poly-6a

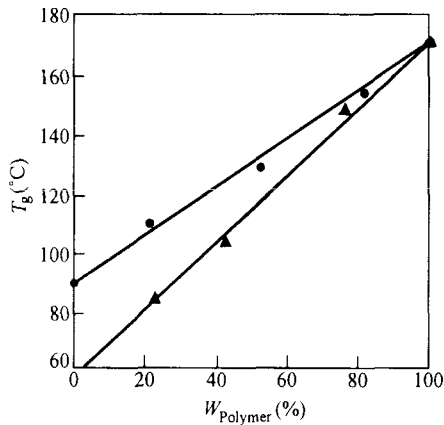


Fig. 4 Glass transition temperatures (T_g) of the polymers in dependence of the azo content [w_{polymer} (%)] in polymers with spacer $\text{---}(\text{CH}_2)_n\text{---}$
 $n=2$ (●), $n=6$ (▲)

Fig.4 presents the glass transition temperatures of the polymers as a function of the content of azo moiety. According to Gorden and Taylor^[20], the glass transition temperatures of the

copolymers can be given by:

$$T_g = W_1 T_{g1} + W_2 T_{g2}$$

where W_1 , W_2 are the weight percentage of comonomers in polymers, while T_{g1} , T_{g2} are the glass transition temperatures of the homopolymers of comonomers respectively. It can be seen from Fig. 4 that with increasing content of azo moiety, the glass transition temperatures of the copolymers increase rapidly, and the experimental results fit the Gordon and Taylor equation very well.

Figure 4 also presents the influence of spacers on T_g . According to Gibbs and Dimarzio^[21], the essence of the glass transition of the polymers is a conformational rearrangement process. The influence of the length of the spacer on T_g of the side-chain polymers lies in the following two aspects: (1) The volume of the side groups increases with increasing length of the spacer which results in the rotational energy of the segment increasing, so T_g increases, (2) The hinder of the rigid mesogen to the rotation of the polymer backbone decreases with increasing length of spacer, so T_g decreases. Considering the two opposite aspects of the spacer on T_g , the factor (2) is dominant for short spacers, whereas for long spacers, factor (1) is dominant. It can be seen from Fig.4 that T_g decreases with increasing the length of the spacer from $-(CH_2)_2-$ to $-(CH_2)_6-$, indicating that the factor (2) is dominant for this series of polymers.

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