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THERMAL BEHAVIOR OF POLYAZOMETHINE-ETHERS HAVING PHENANTHRENE MOIETY IN THE MAIN CHAIN

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Abstract

Eleven types of polyazomethine-ethers were prepared from 2,7-diaminophenanthrene as the amine and 4,4'-diformyl-α,ω-diphenoxyalkanes, 4,4'-diformyl-3,3'-methoxy-α,ω-diphenoxyalkanes and 4,4'-diformyl-3,3'-ethoxy-α,ω-diphenoxyalkanes as the dialdehydes. The polymerization was carried out by stirring the monomers in a mixture of *m*-cresol/*o*-chlorophenol (1:1) for 3 h at room temperature in the dark. The reduced viscosities of polymers were 0.49 to 1.61. The melting temperature (T_m) of the polymer without substituent group was 281°C from 4,4'-diformyl-1,3-diphenoxypropane and then showed a characteristic odd-and-even alternation between even- and odd-numbered carbon chain length in the ethers. The T_m's of the polymers with substituent groups were lower than the linear polymers because of the loose packing as observed for the lower crystallinity. The 10% mass-loss temperatures were 430 K for linear polymers and the lower temperatures were attained for the polymers with substituent groups.

Keywords: 1,7-diaminophenanthrene, differential scanning calorimetry, 4,4'-diformyl-3,3'-ethoxy-α,ω-diphenoxyalkane, 4,4'-diformyl-3,3'-methoxy-α,ω-diphenoxyalkane, 4,4'-diformyl-α,ω-diphenoxyalkane, melting temperature, polyazomethine-ether, thermal stability

Introduction

Polyazomethines are prepared by the condensation of diamines with dialdehydes. They have the C=N bonds in the main chain and are conjugated due to their double bonds. Their molecular motions are very restricted except for the *cis–trans* isomerization and the rotation of nitrogen atoms. Therefore, polyazomethines are expected as the functional polymers, which have high thermal stability, high strength and modulus, liquid crystallinity, electric conductivity and piezoelectricity.

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Various types of polyazomethines have been synthesized by the condensation of aromatic dialdehydes with aromatic and/or aliphatic diamines. Morgan *et al.* [1] synthesized a number of fusible polyazomethines that can be spun into fibers by a melt process. Li and Chang [2–4] prepared polyamide-polyazomethines with long methylenes in the main chain using *m*-cresol/*o*-chlorophenol as solvent and reported the liquid crystallinity.

In this report, we synthesized polyazomethine-ethers (Scheme 1) from 2,7-diaminophenanethrene as the diamine and 4,4'-diformyl-α,ω-diphenoxyalkanes, 4,4'-diformyl-3,3'-methoxy-α,ω-diphenoxyalkanes and 4,4'-diformyl-3,3'-ethoxy-α,ω-diphenoxyalkanes as the dialdehyde and clarified their thermal stability.

Experimental

Monomers

2,7-Diaminophenanthrene was prepared from 2,7-dibromophenanthrene.

4,4'-Diformyl-α,ω-diphenoxyalkanes were prepared [3] by dissolving 4-hydroxybenzaldehyde (2.12 g, 20 mmol), α,ω-dibromoalkane (10 mmol) and sodium carbonate (2.08 g, 25 mmol) in DMF (8 mL) and stirring for 4 h at 150°C. After the reaction, reaction mixture was poured in the water (200 mL) and the precipitated crystals were filtered. The crude crystals were dissolved in chloroform and washed with a 1.5 N sodium hydroxide solution and then water and dried with magnesium sulfate.

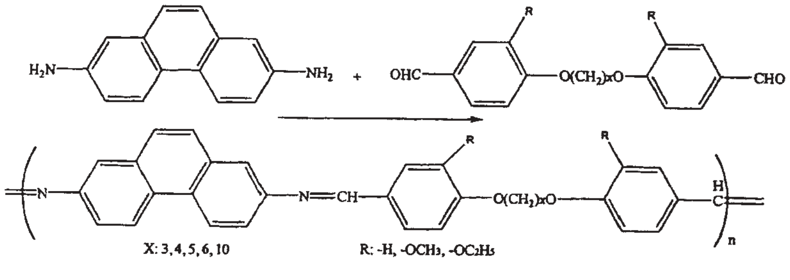
4,4'-Diformyl-3,3'-methoxy-α,ω-diphenoxyalkanes were prepared similar to that described above [3] except that vanillin was used instead of 4-hydroxybenzaldehyde.

4,4'-Diformyl-3,3'-ethoxy-α,ω-diphenoxyalkanes were prepared similar to that described above [3] except that ethyl vanillin was used.

The products were fine white crystals and the yields were 63–85%. The purity of the products was confirmed by measuring *m.p.*, IR and ^{1}H-NMR.

Polymerization

1,7-Diaminophenanthrene (1 mmol) was allowed to react with diphenoxyalkanes (1 mmol) in a mixture (1:1) of *m*-cresol/*o*-chlorophenol (4 mL) by stirring for 3 h at room temperature in the dark. After the reaction, the solution was poured in methanol. The precipitated polymer was filtered and washed with methanol.



Scheme 1 Polyazomethine-ethers

The polymer purified was yellowish powder. Reduced viscosity and IR spectrum were measured for each polymer.

Characterization

The melting points were measured on a Mitamura Mel-Temp II melting point apparatus. IR spectra were recorded with a Jasco IR-810 grating IR spectrophotometer on KBr disks. Solution viscosities were determined at 0.2 g dL^{-1} concentration in methanesulfonic acid at 30°C using an Ostwald viscometer.

The phase transition temperatures were determined by a Perkin Elmer DSC system 4 at a heating rate of 10 K min^{-1} under nitrogen. The thermal stability was examined with a Seiko TG/DTA 200 at a heating rate of 10 K min^{-1} under nitrogen. Dynamic viscoelasticity was measured with a Seiko DMS 210 at a heating rate of 10 K min^{-1} under nitrogen and in a frequency of 0.01–20 Hz.

Wide-angle X-ray diffraction diagrams were taken on powder specimens with a Rigaku Geigerflex Rad-γ A X-ray diffractometer using nickel-filtered CuK$_\alpha$ radiation (40 kV, 100 mA).

Results and discussion

The results of polymerization of polyazomethine-ethers are given in Table 1 together with the codes, the number of carbon atoms and the substituent groups and the melting points of the dialdehydes.

The polycondensation proceeded almost quantitatively. In the IR spectra of polymers, a strong absorption due to azomethine bond was observed at 1620 cm^{-1}. The absorption due to carbonyl group in the formyl group was not observed. Therefore, the formation of polyazomethine-ether was confirmed.

Polyazomethine-ether obtained was not soluble in usual solvents or aprotic polar solvents, soluble in *m*-cresol, *o*-chlorophenol, trifluoroacetic acid or phenol/1,1,2,2-tetrachloroethane (6:4) and soluble in concentrated sulfuric acid and methanesulfonic acid. Therefore, methanesulfonic acid was used for viscosity measurements.

The X-ray diffraction patterns of polymers were recorded. The X-ray diffraction pattern of the linear polymers are sharp and the crystallinity is high, whereas the X-ray diffraction patterns of polymers with substituent groups were broader because of the lower packing density due to the substituent groups. The X-ray diffraction pattern of linear polymer $\underline{2}$ (x= 4) and that of branched polymer $\underline{6}$ with methoxyl groups (x= 4) are shown in Fig. 1.

Thermal stability of polyazomethine-ethers under nitrogen was determined by TG/DTA and the melting temperature was determined by DSC. The results are shown in Table 2.

The 10% mass-loss temperatures (DT_{10}'s) of linear polyazomethine-ethers are 430°C and the residual masses at 500°C are 44 to 66%. These results indicate that polyazomethine-ethers have the excellent thermal stability. However, the polymers with substituent groups have lower DT_{10}'s.

Table 1 Synthesis of polyazomethine-ethers[a]

Code	*x*	*R*	Diphenoxyalkane *m.p.*/°C	Polymer	
				Yield/%	η_{rel}[b]/dL g^{-1}
1	3	H	125–127 (125–127[3])	93.8	0.88
2	4	H	102–103 (104–106[3])	97.8	1.61
3	5	H	77–79 (77–78[3])	92.8	0.49
4	6	H	101–102	92.9	1.03
5	10	H	79–80 (80–81[3])	96.3	0.52
6	4	OCH_3	157–158 (158–160[3])	90.4	1.19
7	6	OCH_3	159–161 (162–163[3])	92.8	0.93
8	10	OCH_3	100–101 (98–99[3])	90.3	1.06
9	4	OC_2H_5	138–140	94.2	1.21
10	6	OC_2H_5	88–89	93.3	0.91
11	10	OC_2H_5	125–127	90.0	0.74

[a] Polymerization was carried out with 1 mmol of each monomer in 4 mL of *m*-cresol/*o*-chlorophenol (1:1) at room temperature for 3 h

[b] Measured at a concentration of 0.2 dL g^{-1} in methanesulfonic acid at 30°C

Table 2 Thermal properties of polyazomethine-ethers

Code	T_m[a]/°C	DT_5[b]/°C	DT_{10}[c]/°C	RW[d]/%
1	281	424	433	66
2	382	422	433	56
3	255	419	430	54
4	334	421	433	52
5	294	422	431	44
6	334	379	391	56
7	304	384	393	52
8	264	385	392	42
9	257	395	403	55
10	246	396	403	47
11	254	342	369	44

[a] Determined at a heating rate of 10 K min^{-1}

[b] A 5% mass-loss temperature determined at heating rate of 10 K min^{-1} under N_2

[c] A 10% mass-loss temperature determined at heating rate of 10 K min^{-1} under N_2

[d] Residual mass at 500°C determined at heating rate of 10 K min^{-1} under N_2

The melting temperature (T_m) of polymers shows characteristic odd-and-even alternation between even- and odd-numbered carbon chain length in the ethers (Fig. 2). The T_m of x=3 is 281°C and that of x= 4 is 382°C.

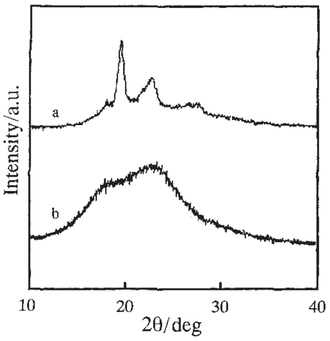


Fig. 1 X-ray diffraction patterns of polyazomethine-ethers. a – linear polymer 2 (x=4); b – branched polymer with methoxyl groups 6 (x=4)

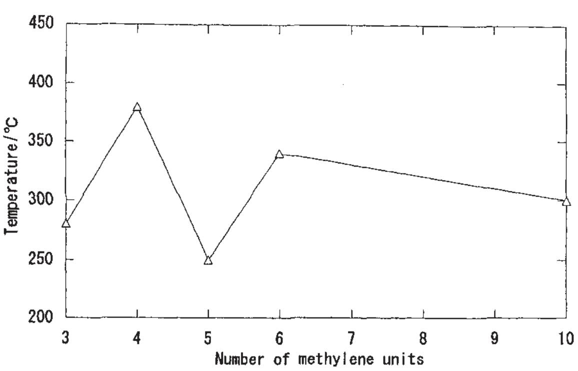


Fig. 2 Melting temperatures of linear polyazomethine-ethers. Heating rate: 10 K min^{-1}

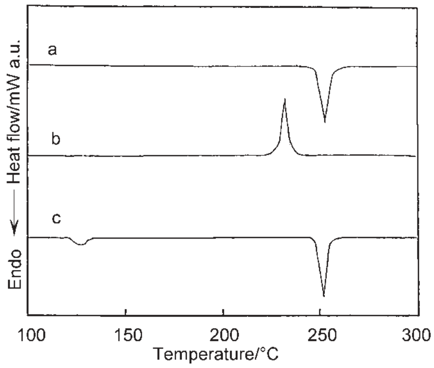


Fig. 3 DSC curves of polyazomethine-ether 9. a – First heating. Heating rate: 10 K min^{-1}, b – First cooling. Cooling rate: 10 K min^{-1}, c – Second heating. Heating rate: 10 K min^{-1}

For the T_m of the polymers with substituent groups, the lowering of melting temperature is particularly remarkable. This decrease of melting temperature is explained again by the lowering of packing density of the polymer main chain due to the intro-

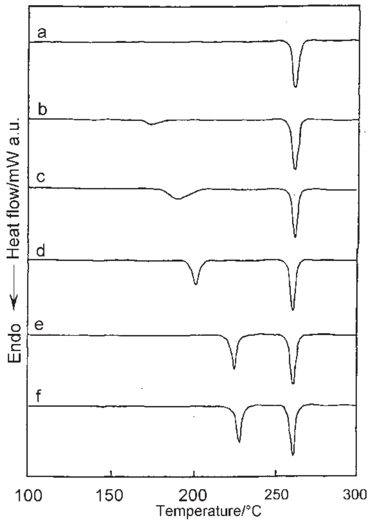


Fig. 4 Heat treatment of polyazomethine-ether 9 at 200°C under vacuum. a – 0 min, b – 5 min, c – 10 min, d – 15 min, e – 30 min and f – 60 min

duction of the substituent groups and the resulting twisting of the planar structure of polymer main chain.

The DSC curves of polyazomethine-ether 9 with methoxyl groups are shown in Fig. 3. An endothermic peak due to melting was observed at 257°C in the 1st heating and, for the 1st cooling, an exothermic peak due to crystallization was observed at 220°C. In the 2nd heating, a small endothermic peak at 120°C was observed in addition to the melting peak.

Table 3 Heat treatment of polyazomethine-ether 9

Heat treatment[a]/ min	η_{rel}[b]/dL g^{-1}	T_{m_1}[c]/°C	T_{m_2}[c]/°C
0	1.21	–	257
5	1.39	172	257
10	1.71	186	257
15	2.36	201	257
30	–[d]	223	257
60	–[d]	227	257

[a] Heat-treated at 200°C at vacuum
[b] Measured at a concentration of 0.2 g dL^{-1} in methanesulfonic acid at 30°C
[c] Determined at a heating rate of 10 K min^{-1}
[d] Insoluble

Therefore, the polymer 9 was heat-treated at 200°C in vacuo and the DSC curve was recorded (Fig. 3). The melting temperature was not affected by the heat treatment. The lower temperature peak shifted to higher temperature and became larger and sharper with heat treatment. However, the effect of heat treatment was almost finished after 30°C (Fig. 4).

With heat treatment the reduced viscosity was increased and the polymer became insoluble in any solvent after 30 min (Table 3). From the IR spectra the absorption due to the carbonyl group of formyl group in the polymer chain ends decreased and that due to the azomethine group increased. The polyazomethine has the C=N bond in the main chain and the cross linking is expected as the effects of heat and light.

Conclusions

Polyazomethine-ethers were prepared from 2,7-diaminophenanthrene and 4,4'-diformyl-3,3'-ethoxy-α,ω-diphenoxyalkanes. A characteristic odd-and-even alternation of the melting temperature (T_m) was observed between even- and odd-numbered carbon chain length in the ethers. The 10% mass-loss temperatures of these polymers were 430 K. When the α,ω-diphenoxyalkanes were substituted with 3,3'-methoxy and 3,3'-ethoxy groups, the melting temperature (T_m) and the 10% mass-loss temperatures became lower.

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