

STUDIES ON THE REGULAR COPOLYMERS OF POLY (1, 4-PHENYLENETEREPHTHALAMIDE)

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ABSTRACT

Two types of the regular copolymer of poly (1, 4-phenyleneterephthalamide) were synthesized by the low temperature solution polycondensation in NMP- CaCl_2 solvent system, using the piperazine or 2, 5-dimethylpiperazine as the third components introduced in the main chain of poly (1, 4-phenyleneterephthalamide). The properties of copolymers were characterized by IR, SEM, X-RAY diffraction, polarizing microscopy, TGA and solubilities.

Experimental results showed that the copolymers had good solubility and thermal stability, the concentrated sulfuric acid ($\sim 98\%$) solution of regular PPTA copolymers had liquid crystalline properties.

INTRODUCTION

Aromatic polyamide, poly (1, 4-phenyleneterephthalamide) (PPTA) has highly extended chain conformations, therefore exhibits high thermal stability and poor solubility. PPTA can form anisotropic liquid crystalline solutions^[1,2]. Fibers with high tenacity and high modulus can be obtained by spinning this kind of polymer solution^[3]. However, their behavior under compression is poor^[4].

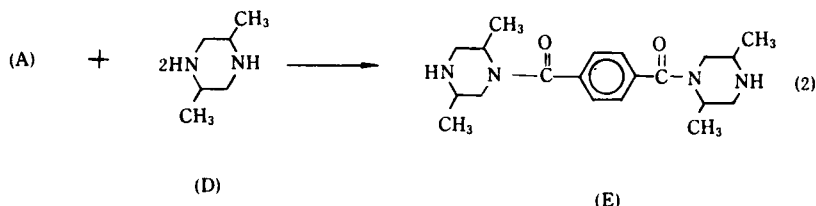
Polypiperazinamides were prepared by interfacial and solution polycondensation^[5-8]. Anisotropic membranes were prepared from poly (trans-2, 5-dimethylpiperazin-thiofurazanamide)^[9].

This paper describes the using of piperazine or 2, 5-dimethylpiperazine as the third components which have been introduced in the main chain of poly (1, 4-phenyleneterephthalamide) with regular position for improving the solubility and flexibility of PPTA.

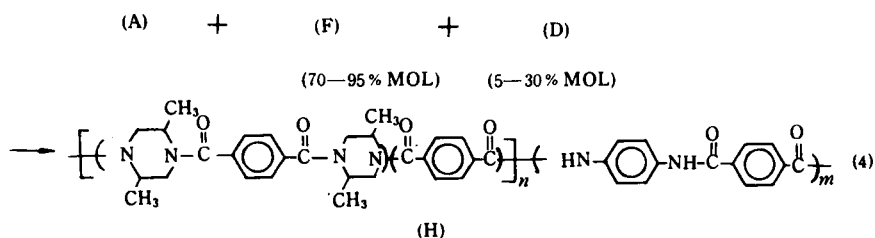
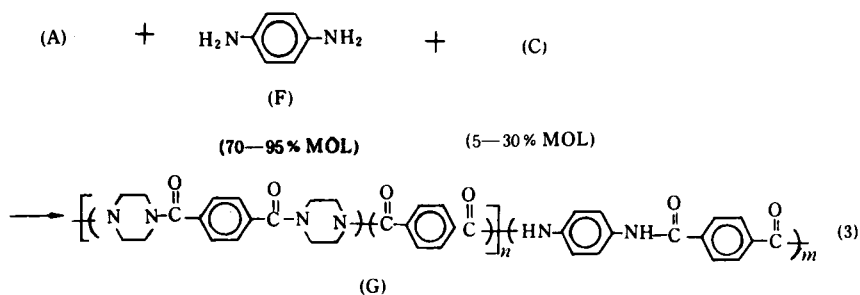
EXPERIMENTAL

1. Materials

The following two monomers were used without further purification; Piperazine (Aldrich) and 2, 5-dimethylpiperazine (Aldrich). While the monomer 1, 4-phenylenediamine; which was obtained commercially, was purified by vacuum distillation to white solids (melting point $140 - 141^\circ\text{C}$). Terephthaloyl chloride was prepared by refluxing the mixture of terephthalic acid, thionyl chloride, and a small amount of dimethylformamide. The white terephthaloyl chloride with a melting point $83 - 84^\circ\text{C}$ were obtained by twice vacuum distillation. CaCl_2 was dried at 350°C for 3hrs. N-methylpyrrolidone (NMP) was stored over type 4A molecular sieves and vacuum distilled over sodium hydroxide pellets.



STEP 2



Two types of the regular copolymer of poly (1,4-phenyleneterephthalamide) were synthesized by low temperature solution polycondensation in NMP-CaCl₂ solvent system. Piperazine or 2,5-dimethylpiperazine used as the third components. were introduced in the main chain of poly (1,4-phenyleneterephthalamide) with regular position.

Effect of the percentage of third components on the inherent viscosity of the regular copolymers of poly (1,4-phenyleneterephthalamide) is shown in Fig. 1. The curve 1 is PPTA-2,5-dimethylpiperazine copolymer in regular (PM), the curve 2 is PPTA-piperazine copolymer in regular (P), the curve 3 is PPTA-2,5-dimethylpiperazine copolymer in random (PMN), the curve 4 is PPTA-piperazine copolymer in random (PN). Experimental results show that the inherent viscosity of copolymers decreased with increasing of the mol % content of third components. The inherent viscosity of regular copolymers were higher than that of random copolymers. However, the inherent viscosity of PPTA-2,5-dimethylpiperazine system were higher than that of PPTA-piperazine system, whichever the copolymers are of regular or random.

2. IR spectrum of PPTA-piperazine copolymer

IR spectrum of PPTA-piperazine copolymer is shown in Fig. 2. The spectrum of PPTA-piperazine copolymer shows the N—H stretching vibration at 3300 cm⁻¹; and three characteristic absorptions attributable to amide I, II, III bands of PPTA

at 1650 cm^{-1} ($\text{C}=\text{O}$ stretching), 1545 cm^{-1} (CNH), and 1250 cm^{-1} (CNH), respectively. The $\text{H}-\text{CH}$ stretching vibration at $2850-2930\text{ cm}^{-1}$ is distinctive for the cyclic methylene groups in the polymers that indicates the presence of piperazine groups in the copolymer.

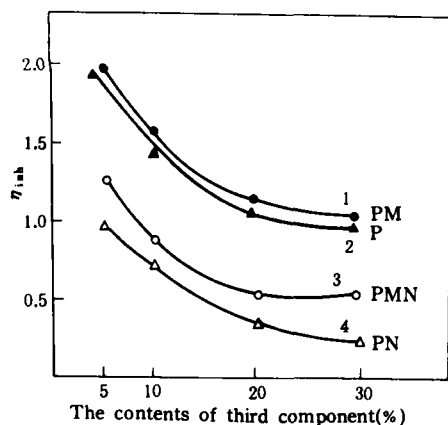


Fig. 1 Effect of the content of third component on η_{inh} of PPTA copolymers

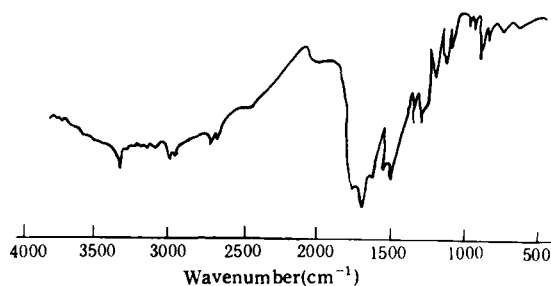


Fig. 2 IR spectrum of PPTA-piperazine copolymer

3. Thermo-gravimetric analysis (TGA) of copolymers.

The results of TGA for the 30 mol % third components are shown in Table 1. Experimental results show that the thermostability of PPTA-regular copolymers are better than that of the random copolymers.

The thermostability of PPTA-piperazine system or PPTA-2,5-dimethyl-piperazine system all decreased with increasing mol percentage content of third components in copolymers.

When the weight loss is the level of 10%, the thermostability of most copolymers except for PM-PPTA are keeping to above 300°C , even though 30 mol% of the third components are introduced in the PPTA main chain.

Table 1 Thermal stability of copolymers

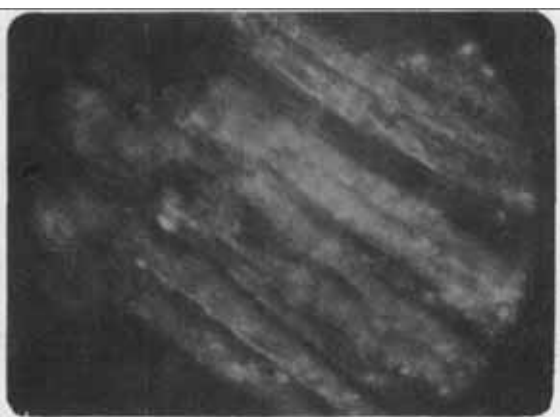
Loss wt %	Thermal stability ($^\circ\text{C}$)			
	Regular	Copolymer	Random	Copolymer
	P-PPTA	PM-PPTA	P-PPTA	PM-PPTA
10%	360	320	330	250
20%	440	370	410	280
30%	520	420	500	410
50%	590	570	570	570

4. Liquid crystalline property of copolymers

Typical mat-like optical texture of nematic state^[7] was observed on cross-polarizing microscope for both shearing-oriented film, which was prepared from the sulfuric acid ($\sim 98\%$) solution of copolymers (12% by weight). Fig. 3 (A) is the PPTA copolymer which contains 30 mol % piperazine, Fig. 3 (B) is

the PPTA copolymer which contains 20 mol % 2,5-dimethylpiperazine. When the conc. sulfuric acid solution of copolymer which contains 30 mol% 2,5-dimethylpiperazine (12% by weight) was tested under cross-polarizing microscope, no liquid crystalline feature was observed.

Experimental results show that the liquid crystalline properties of PPTA-piperazine system copolymers are much better than that of the PPTA-dimethylpiperazine system.



(A)

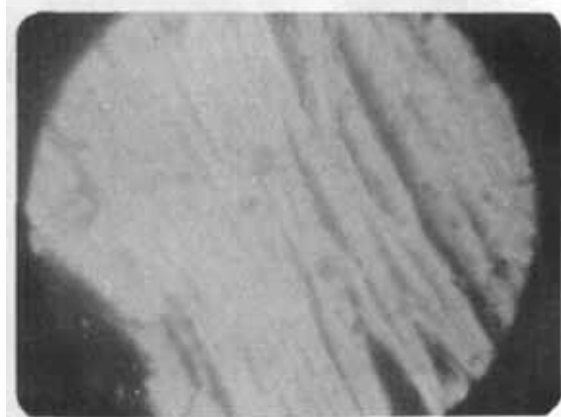


Fig.3 Polarizing micrograph of copolymers

(A) PPTA-30 mol % piperazine copolymer (B) PPTA-20 mol % 2,5-dimethylpiperazine copolymer

5. Solubility of copolymers

The results obtained for solubility of two kinds of copolymers are given in Table 2, showing that the solubility of PPTA copolymers are better than pure

Table 2 Solubility of copolymers

Polymer	Solvents				
	H ₂ SO ₄	HCO ₂ H	NMP - CaCl ₂	DMAC - HMPA	DMSO
P 5%	++	+-	+Δ+	+-	+-
P 10%	++	+-	+Δ+	+-	+-
P 20%	++	++-	++	+-	+-
P 30%	++	++-	++	+-	+-
PM 5%	++	+-	++-	+-	+-
PM 10%	++	+-	++-	+-	+-
PM 20%	++	+-	++-	+-	+-
PM 30%	++	++-	++-	+-	+-
PN 30%	++	+-	--	+-	+-
PMN 30%	++	+-	--	+-	+-
PPTA	++	--	--	--	--

Notes: ++ soluble ++- little insoluble +- little soluble +- - swell +Δ+ heated soluble -- insoluble

P=PPTA-piperazine copolymer in regular

PM=PPTA-2,5-dimethylpiperazine copolymer in regular

PMN=PPTA-2,5-dimethylpiperazine copolymer in random

PN=PPTA-piperazine copolymer in random

PPTA, and the solubility of PPTA regular copolymers are better than that of the PPTA random copolymers. The solubility order in these copolymers is as follows:

PPTA regular copolymer > PPTA random copolymer > PPTA

6. X-Ray diffraction of copolymers

The intensity curves of the wide-angle X-Ray diffraction of two system PPTA powdered copolymers are given in Fig.4 and 5. In Fig.4, the curve 1 and curve 5 are the PPTA-copolymer which contains 30 mol% piperazine, curve 1 is the PPTA-piperazine random copolymer and curve 5 is the PPTA-piperazine regular copolymer. The curves 2, 3, 4 of Fig.4 are the PPTA-piperazine regular copolymers which contains 5%, 10%, 20% mol piperazine respectively. In Fig.5 the curves 2, 3, 4, and 5 are the PPTA-2,5-dimethylpiperazine regular copolymers which contain 5%, 10, 20% and 30 mol% 2,5-dimethylpiperazine respectively. The results of Fig.4 and Fig.5 show that the two systems PPTA-copolymer all reveal five peaks at 2θ being nearly 17° , 20° , 23° , 25° and 27° . The two peaks at 2θ near 20° and 23° , are the typical PPTA peaks which depend on the quantity of the third component introduced into the PPTA main chain, the intensity of two peaks decrease with increasing the mol percentage content of third components. In Fig.5 curve 4 and curve 5 showed that the peak of 2θ near 20° is almost disappeared, when the mol percentage of 2,5-dimethylpiperazine over 20%. Experimental results also show that the crystallinity of regular copolymer is better than the crystallinity of random copolymer.

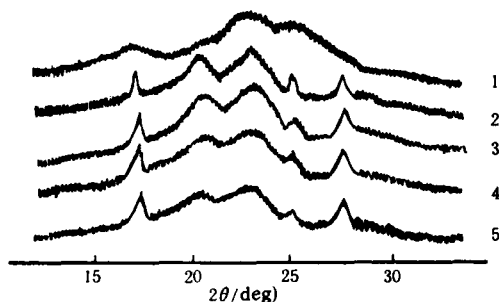


Fig.4 The intensity curves of wide-angle X-ray diffraction of PPTA-piperazine copolymers

(1) 30% PN (2) 5% P (3) 10% P (4) 20% P
(5) 30% P

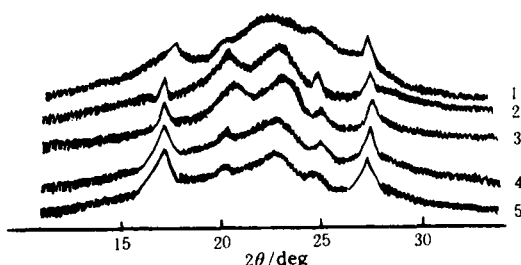


Fig.5 The intensity curves of wide-angle X-ray diffraction of PPTA-2,5-dimethylpiperazine copolymers

(1) 30% PMN (2) 5% PM (3) 10% PM
(4) 20% PM (5) 30% PM

7. Morphology of copolymers

The scanning electron micrographs (SEM) of two system PPTA powdered copolymers are given in Fig.6 and 7. Fig.6 shows the SEM of PPTA-piperazine copolymers system. The results of Fig.6 and 7 showed that the apparent micrographs of regular copolymers Fig.6 (b) and Fig.7 (b) are looser than random copolymers Fig.6 (a) and Fig.7 (a), therefore the solubility of the PPTA regular copolymers are better than the PPTA random copolymers.

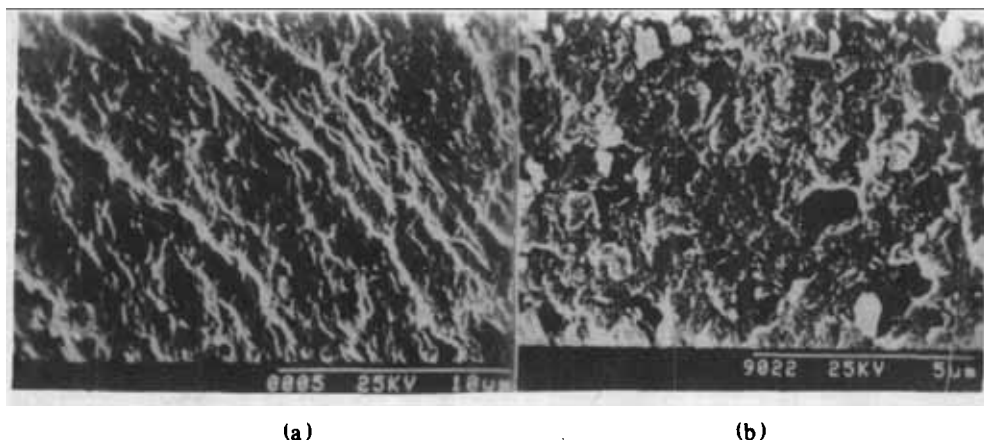


Fig.6 The Scanning Electron Micrographs of PPTA-piperazine copolymers
(a) 30% PN; (b) 30% P

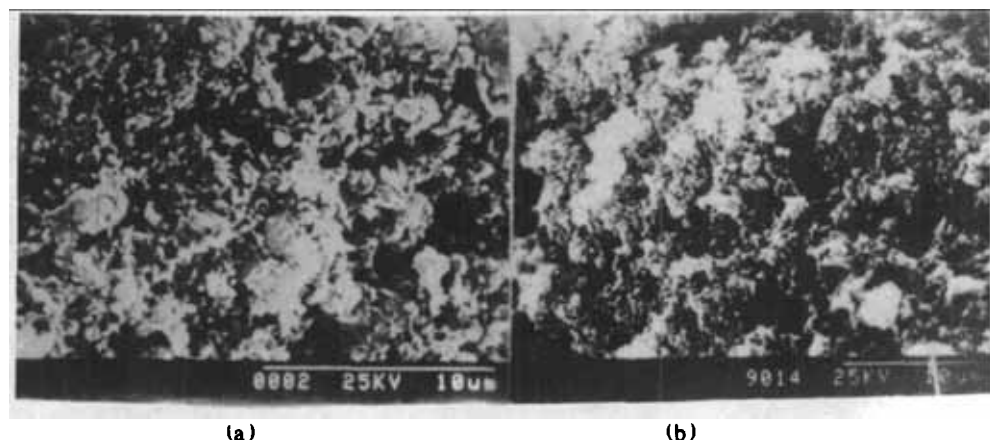


Fig.7 The Scanning Electron Micrographs of PPTA-2,5-dimethylpiperazine copolymers
(a) 30% PMN; (b) 30% PM

Keywords :

Poly (1,4- phenyleneterephthalamide) ; Aromatic copolyamide ; Piperazine ; 2,5-Dimethylpiperazine liquid crystalline polymer

REFERENCES

- [1] Blades , H., *U.S.Pat.* , 1973 , 3 , 767 , 756 and 1975 , 3 , 869 , 429 .
- [2] Kikuchi , J., *J. Textile Mach. Soc. Jpn.* , 1974 , 12 , 27 and 722 .
- [3] Wilfong , R.E. , *J. Appl. Polym. Sci.* , 1977 , 31 , 1 .
- [4] Takayanagi , M. , *J. Macromol. Sci. Phys B.* , 1983 , 17 , 591 .
- [5] Morgan , P.W. , "Condensation Polymers : by Interfacial and Solution Method" , Interscience , N.Y. , 1965 .
- [6] Mortillaro , L.; Russo , M.; Guidotti , V. and Credali , L., *Makromol. Chem.* , 1970 , 151 , 138 .
- [7] Guidotti , V.; Russo , M. and Mortillaro , L. , *Makromol. Chem.* , 1971 , 111 , 147 .
- [8] Bao , Jingsheng and Yang , Xijian , 合成纤维工业 (*Synthetic Fibre Industry*) , 1981 , 4 , 1 .
- [9] Credali , L.; Chiolle and Parrini , P., *Polymer Materials for RO Membranes Desalination* , 1974 , 14 , 137 .
- [10] Chen , Shouxi ; Long , Changfen and Cai , Liying , 高分子通讯 (*Polym. Commun.*) 1981 , 4 , 24 .