Preparation of a novel oxalic-aromatic copolyamide-hydrazide

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A novel copolyamide-hydrazide having aromatic as well as aliphatic units has been synthesized by low temperature solution polycondensation of oxalylodihydrazide and *p*-aminobenzohydrazide with terephthaloyl chloride in *N*,*N*-dimethylacetamide containing dissolved lithium chloride. Its intrinsic viscosity was 2.06 dl g^{-1}. Differential thermal analysis and thermal gravimetric analysis were carried out and the mechanical properties of the copolymer were investigated.

(Keywords: copolyamide-hydrazide; polycondensation; block copolymer; synthesis)

INTRODUCTION

Wholly aromatic polyamide-hydrazides have been investigated extensively as potential high performance materials with high thermal stability[1]. Several properties of the polyamide-hydrazides such as thermo-oxidative stability[2], high mechanical strength and moduli[3], and reverse osmosis applications[2,4–7] have been established.

There is not much literature available on the aliphatic-aromatic polyamide-hydrazides[8], and the present study deals with work carried out on a polyamide-hydrazide that was synthesized from aliphatic and aromatic monomers. This has an inherent advantage over purely aliphatic or purely aromatic polymers since one can expect flexibility and hence low temperature stability to be provided by the aliphatic part of the copolymer. At the same time, the aromatic part of the copolymer should provide the ability to withstand higher temperatures.

EXPERIMENTAL

Materials

p-Aminobenzohydrazide (PABH), oxalylodihydrazide (ODH), terephthaloyl chloride (TCl), lithium carbonate, calcium hydride, *N*,*N*-dimethylacetamide (DMAc) and lithium chloride (LiCl) were extra pure reagents obtained from Nacalai Tesque Inc., Japan. DMAc was dried over calcium hydride followed by distillation under reduced pressure and stored over molecular sieves prior to use. LiCl was dried for 10 h at 170–200°C before use.

Copolymer synthesis

A 250 ml four-necked round-bottom flask was equipped with mechanical stirrer, nitrogen inlet tube and a thermometer. Then PABH (1.51 g, 0.01 mol), ODH (1.18 g, 0.01 mol) and dry DMAc (100 ml) containing LiCl (0.5 g) were added and stirred under dry nitrogen atmosphere until complete dissolution. The contents were cooled to -5°C. After 30 min, TCl (4.06 g, 0.02 mol) was added slowly with constant stirring over a period of 2 h. After this, the reaction was continued at -5°C for a further 2 h. The reaction temperature was then raised to room temperature and maintained for $\sim$18 h with stirring under nitrogen atmosphere. The reaction mixture was then neutralized with lithium carbonate (1.46 g, 0.02 mol), warmed to $\sim$70–80°C and stirred at this temperature for no less than 2 h, degassed under vacuum and filtered through a sintered glass funnel. A sample of the filtrate was precipitated in methanol, filtered and dried in a vacuum oven at 75°C to constant weight. The remaining filtrate was used for film preparation. The yield of the dry product was 5.1 g (96.4%). Film was prepared by casting a polymer solution on a glass plate followed by thermal treatment at 110°C near to dryness. The film was then immersed into methanol to allow the complete extraction of solvent and additives (inorganic salt; LiCl) and finally dried to constant weight.

Copolymer characterization

The intrinsic viscosity of a 0.5% solution of copolymer in DMAc was determined at 25 ± 0.5°C. The i.r. spectrum was recorded on a Shimadzu Fourier transform infrared spectrophotometer FTIR 4200. D.t.a. and t.g.a. measurements of the copolymer were performed on a Daini Seikosha thermal analyser at a heating rate of 10°C min^{-1}. The X-ray diffractogram was obtained using a Rigaku Denki refractometer RAD-B system. The tensile strength, elongation-to-break and elastic modulus of the copolymer film were measured on a Shimadzu autograph.

RESULTS AND DISCUSSION

Oxalic-aromatic copolyamide-hydrazide was prepared by the reaction of PABH (50 mol%) and ODH (50 mol%) with a stoichiometric amount of TCl in DMAc containing LiCl. The HCl by-product may be expected to act as a reaction catalyst and form complexes with the DMAc solvent[9]; this complexation should shift

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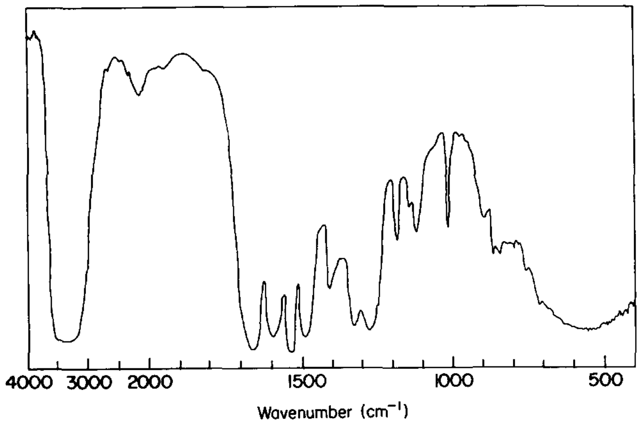
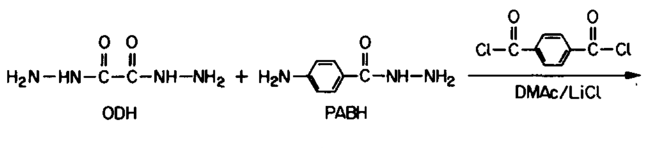
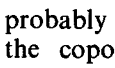


Figure 1 I.r. absorption spectrum of (PABH/ODH)–TCl copolymer



Scheme 1

the polymerization equilibrium towards completion. Addition of LiCl to the polymerization medium enhances the solubility of the copolymer. Although there is competition between the copolymer and solvent (DMAc) for the Li^+ cation, the solvent is more basic than the polymeric product. Binding by the solvent predominates and the Li^+ cation associates with the solvent carbonyl oxygen; this is useful for making and retaining the oxalic-aromatic polyamide-hydrazide in solution. Since the polymerization solution is highly acidic, it is common practice to add lithium carbonate to neutralize the HCl formed and to produce a soluble salt (i.e. LiCl), which is often more effective as the copolymer solubilizer.

The i.r. spectrum of the copolymer is shown in *Figure 1*. The copolymer exhibited a broad band at 3600–3100 cm^{-1} due to interchain hydrogen bonding (=N–H···O=C= stretching). The carbonyl stretching frequency of 'amide I'  $\left(\begin{array}{c}\mathrm{H}\ \ \mathrm{O}\\ |\ \ \ \|\\ -\mathrm{N}{-}\mathrm{C}-\end{array}\right)$ was observed at 1660–1640 cm^{-1}.

Based on the elemental analysis data of the copolymer (C, 51.37%; H, 3.74%; N, 16.36%; O, 28.53%), it cannot be assumed that the copolymer is wholly random owing to the difference in reactivity between PABH and ODH toward TCl. Moreover, the rate of reaction of the hydrazide group with acid chloride is seven times faster than that of the amino group[10,11]. Thus, there are probably blocks of PABH–TCl and ODH–TCl within the copolymer chain as represented by *Scheme 1*. However, no evidence for such blocks has been reported.

The intrinsic viscosity of the copolymer was 2.06 dl g^{-1} and besides being soluble in DMAc, the copolymer was also soluble in dimethyl sulfoxide, *N*-methyl pyrrolidone and hexamethyl phosphoramide.

The X-ray diffractogram of the copolymer indicates that it is semicrystalline due to the presence of *p*-oriented phenylene rings incorporated into the copolymer chains.

The tested copolymer had a tensile strength of 406.4 kg cm^{-2}, an elongation-to-break of 1.12% and an elastic modulus of 3.94×10^4 kg cm^{-2}.

The differential thermograms of the copolymer studied showed two broad and intense endotherms. The first occurred between 100°C and 170°C due to loss of adsorbed surface water and the second between 200°C and 400°C due to the cyclodehydration reaction during which the copolymer converted into the corresponding poly(amide-oxadiazole)[1,2,12].

T.g.a. thermograms are shown in *Figure 2*. In both degradation atmospheres, the copolymer showed the same characteristic behaviour. This consisted of: relatively small weight losses (~2%), which occurred between 100°C and 200°C due to evaporation of adsorbed moisture and solvent; considerable weight losses (~19%), which occurred between 200°C and 400°C owing to the cyclodehydration reaction by which 1,3,4-oxadiazole rings were formed from the hydrazine linkages and during which H_2O was lost; and the degradation of the poly(amide-oxadiazole), which started at 460°C.

From the above results, it is interesting to note that weight loss during the cyclodehydration reaction of oxalic acid containing polyamide-hydrazide (the copolymer studied), 16–19% H_2O, is larger than that of wholly aromatic polyamide-hydrazide (6% H_2O)[12]. This result is consistent with the observation of Frazer and Wallenberger[13]. They tested the cyclodehydration reaction of the oxalic acid containing polyhydrazides and proposed a different polyoxadiazole structure containing adjacent oxadiazole rings, as represented by *Scheme 2*, that separate the aromatic portions. Moreover, these differences in reactivity and structure make it advisable to distinguish between aliphatic and aromatic polyamide-hydrazides and those containing oxalic acid.

CONCLUSIONS

An easily processed, new oxalic-aromatic copolyamide-hydrazide was successfully prepared as a viscous film forming solution. It was characterized by high thermal stability and good mechanical properties.

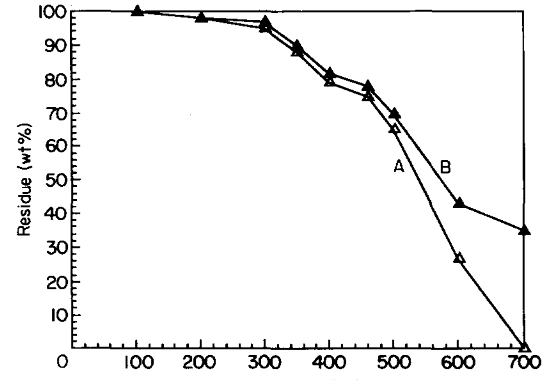
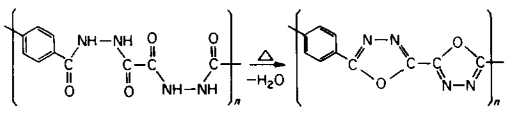


Figure 2 T.g.a. of (PABH-ODH)–TCl copolymer: (A) in air; (B) in nitrogen



Scheme 2

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