polymer communications

High performance polymers prepared by transformation of processable polyamides

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A new route to the preparation of films and fibres of intractable rigid-rod molecules is described. Aromatic polyamide systems are prepared with varying levels of alkyl-based side-chain substitution, which leads to materials with good solubility in standard solvents such as tetrahydrofuran. The chemical structure and the physical properties of such materials may be transformed by cleavage of the solubilizing side-chains in the solid state. Films prepared in this manner are insoluble and intractable.

(Keywords: high performance polymers; aromatic polyamide; transformation)

Introduction

Polymeric materials with high levels of molecular orientation can exhibit high mechanical moduli[1]. Such properties are displayed by extended-chain systems and arise from the relative stiffness of covalent bonds when directly distorted. There are two principal routes to these technologically useful materials: the first involves extending and organizing flexible chain systems[2]; the second centres on the use of stiff aromatic-based polymer molecules[3]. It is a fundamental problem of polymer science that potentially useful molecular materials, which might exhibit excellent mechanical properties or high electrical conductivities, are essentially insoluble and intractable through their inherent stiffness. Clearly, that intractability inhibits the organization of such stiff molecules into useful structures. One approach to circumvent these problems has been to utilize a tractable precursor which is organized and then transformed into the final material. The viscose process[4], in which cellulose is solubilized by partial xanthanate formation and reconstituted after spinning, represents the most successful exploitation of this technology. More recent examples of the use of transformable precursors are provided by polyacetylene[5] and poly(vinylphenylene)[6], both of which highlight the often complex chemical requirements inherent in such methodology. In this communication we report a new approach, which utilizes flexible side-chains on an otherwise wholly aromatic system to provide processability in a similar manner to the work of Ballauff[7]. However, such side-chains limit the mechanical properties through the large cross-section per load-bearing chain, and of course such systems do not have good high temperature melting points and structural stability. In our work, the solubilizing side-chains are removed after manipulation of the structure in the final stage of the production process to yield an organized intractable and potentially high performance polymeric material. We have chosen for the base material a copolyamide system in which one monomer has a substantial flexible side-chain, as shown in *Figure 1*. By coupling the side-chain through an ester functionality to the aromatic ring, we provide a facile mechanism for the eventual cleavage of that side-chain.

Materials

Copolymers of the type shown in *Figure 1* were synthesized through a solution polymerization method following the procedures of Salaris *et al.*[8] and Yamazaki *et al.*[9], as shown in *Scheme 1*. *Table 1* lists the essential characteristics of the range of copolymers prepared.

Copolymer composition was evaluated using i.r. spectroscopy, in particular by utilizing the C=O absorption bands at 1655 and 1748 cm^{-1}. Molecular weight data for the copolymers were obtained using gel permeation chromatography with dimethylformamide + 1% w/v LiBr as the eluent, and poly(ethylene oxide) and poly(ethylene glycol) as the standards. The molecular weight and compositional data are listed in *Table 1*.

The materials prepared with a high side-chain content showed diffuse X-ray scattering patterns, typical of non-crystalline systems[10], with a single intense but broad peak at around 1.3 Å^{-1}. The polymers R0 and R25 showed a slightly more structured pattern with peaks at around 1 and 1.8 Å^{-1}, although for all of the materials polarized light microscopy revealed non-birefringent, textureless morphologies. I.r. spectroscopy on each member of the series of polymers showed a broad but intense hydrogen bonded N–H stretching band at around 3300 cm^{-1} which shifted by about +3% in wavenumber and decreased in magnitude on changing the side-chain content from R0 to R100, presumably as a consequence of the long aliphatic side-chains restricting the development of strong hydrogen bonding.

The addition of the flexible side-chains led to an enhanced solubility in common solvents in comparison to the relatively intractable base polymer. This arises both from the role of the side-chains in solution, since the incorporation of side-chains leads to an enhancement

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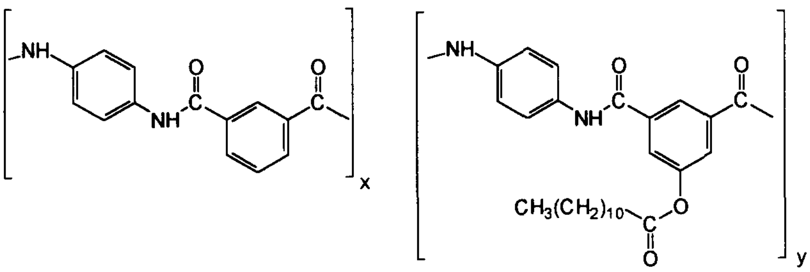
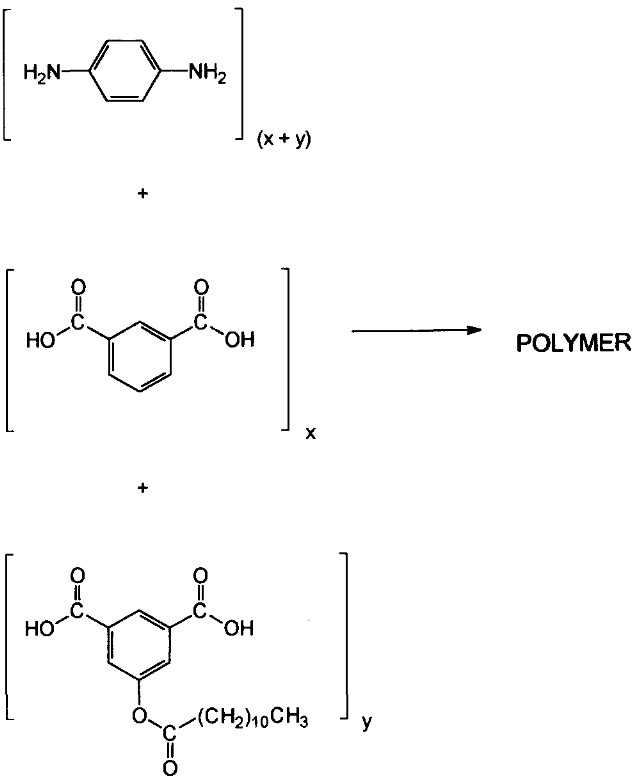


Figure 1 Chemical configuration of the polymers prepared in this work

Table 1 Characteristics of copolymers

Polymer	Feedstock composition	Measured composition[a]	Yield (%)	M_n	M_w	M_w/M_n
R0	0	0	99	–	–	–
R25	0.25	0.26	93	12788	39811	3.11
R50	0.50	0.50	67	16869	38061	2.26
R75	0.75	0.76	84	11778	30000	2.55
R100	1.00	1.00	80	8648	19100	2.21

[a] Obtained by *FT*i.r. spectroscopy; error ±0.05



Scheme 1

of the entropy change at dissolution[7], and from the reduction in the extent of hydrogen bonding in the solid phase. The results of solubility tests are shown in *Table 2*. The rigid-rod systems with a high proportion of side-chains are readily soluble in conventional solvents at modest temperatures, whereas the wholly aromatic system requires salt complexes to provide even minimal solubility in organic amide-based solvents.

Table 2 Results of solubility tests (i, insoluble; p, partially soluble; s, soluble (>2 g/100 ml))

Polymer	THF at 60°C	DMF at 60°C	DMF with LiCl at 60°C
R0	i	i	s
R25	i	p	s
R50	p	s	s
R75	p	s	s
R100	s	s	s

Experimental

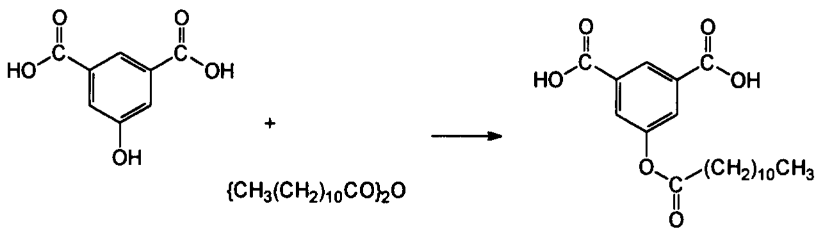
Most of the materials used were commercially available and were used without further purification. The following compounds required additional purification or preparation.

The *p*-phenylenediamine was purified twice by recrystallization from hot water containing 3–3.5% w/v of sodium dithionite and charcoal[10].

Isophthalic acid was purified by recrystallization from hot methanol.

Lauric anhydride was prepared from the reaction of lauric acid with lauroyl chloride[11].

m-Substituted isophthalic acid was prepared by the reaction of 5-hydroxyisophthalic acid with lauryl anhydride, as shown in *Scheme 2*. 5-Hydroxyisophthalic acid (10 g, 0.055 mol) was dissolved in pyridine (35 ml). The yellow solution formed was cooled in an ice-bath until a white solid formed. Lauric anhydride (23 g, 0.06 mol) in tetrahydrofuran (THF) solution (90 ml) was poured into the flask. A solid formed and most of the solvent was removed under vacuum. The remaining solution was stirred for 40 h. The remaining solvent was removed by rotary evaporation. The solid was added to a sulfuric acid solution (50 ml in 100 ml water) and methylenedichloride. The precipitate was filtered and washed with sulfuric acid solution and water. The product was recrystallized twice from aqueous methanol (25% v/v water). The final product was dried in a vacuum oven



Scheme 2

at 65°C for 48 h; the long drying time required was probably due to the formation of a crystal complex with the methanol.

Yield: 15 g (75%); m.p. 173–174°C.

^{1}H n.m.r. (220 MHz, DMSO-d$_6$): $\delta = 0.86$ (3H, t), 1.26 (16H, m), 1.68 (2H, m), 2.64 (2H, t), 7.95 (2H, s), 8.43 (1H, s), 13.52 (2H, bs). I.r. (cm^{-1}): $\nu = 2548, 1767, 1713$. Mass spectrum (CI): $m/z = 364$ (M$^+$).

Typically the copolymerizations were carried out in a mixed solvent of *N*-methylpyrrolidone and pyridine containing 4% w/v LiCl at 85–95°C for 6–7 h. The polymerization reaction was stopped by cooling to room temperature. The resultant polymer was precipitated by the addition of methanol and purified by repeatedly dissolving in dimethylacetamide containing 3% w/v LiCl and precipitating with methanol. Final purification was achieved by Soxhlet extraction using methanol. The purified polymer was dried under reduced pressure. As an example, the synthesis of polymer R0 is described.

In a three-necked round-bottom flask equipped with a thermometer, condenser and magnetic stirrer, *p*-phenylenediamine (2.16 g, 0.002 mol) and isophthalic acid (3.32 g, 0.02 mol) were mixed with *N*-methylpyrrolidone (60 ml) and pyridine (40 ml) containing 4% w/v LiCl as solvent and triphenyl phosphite (10.5 ml, 0.04 mol) as catalyst. Under stirring, a dark-coloured solution was obtained. The temperature was raised to 85–95°C using an oil bath and the solution was maintained at this temperature for 6–7 h. The polymerization was stopped by cooling to room temperature. The raw polymer was purified by dissolving in dimethylacetamide containing 3% w/v LiCl followed by precipitation into methanol. The product was further purified by Soxhlet extraction using methanol as the solvent for 6–8 h and finally dried under reduced pressure for 24 h.

Sample preparation

Two types of sample form were utilized for the transformation stages. The first were uniform thin films which were prepared using a dipping technique which involved withdrawing, at a carefully controlled speed, a prepared substrate from a solution of R100 in THF (6 g/100 mol). The thickness of the film prepared in this manner depends upon the nature of the solvent, the molecular weight and concentration of the polymer, and the speed of withdrawal[12]. The latter provides a useful route to control the film thickness. Typically, a film speed of about 8 mm s^{-1} was used. Single crystals of silicon were utilized as substrates to allow subsequent characterization of the films using Fourier transform i.r. spectroscopy. The spectrum from the polymer was readily obtained by subtracting the i.r. spectrum corresponding to the silicon crystal alone. Typical polymer film thickness was 0.5–3 μm. The second type of samples were in the form of fibres. These were drawn from a concentrated solution of R100 in THF (91 g/100 ml) using a motor-driven pull-off drum providing a draw rate of 0.2–0.5 m min^{-1}. The fibres produced were 1–2 m in length with diameters of 20–30 μm. Scanning electron microscopy showed these materials to be dense with a highly smooth surface.

Transformation

In order to cleave the side-chain attachment through the ester group, the thin films were treated with an aqueous base in the form of 1 N, 2 N and 3 N sodium hydroxide solutions. The films or fibres prepared in the above manner were placed in a universal container with the solution and shaken at 5 Hz for periods ranging from 10 to 1200 min at room temperature. The films were washed three times with water and methylated spirit to remove any by-products of the treatment before further investigations were made. The films were dried at room temperature. Initial experiments showed that the time for complete cleavage depended upon the strength of the base solution. Solution concentrations above 2 N tended to result in damaged films, restricting subsequent spectroscopic analysis, and hence a 1 N solution was selected for the remaining experiments.

Figure 2 shows the i.r. spectra for a thin film of the polymer R100 prior to and after the base treatment. The stretching bands of the carbonyl ester group at 1748 cm^{-1} and the saturated C–H group at 2850–2950 cm^{-1} are not present in the spectra recorded for the transformed sample. Accompanying the disappearance of those bands is the development of a band at around 3300 cm^{-1}, corresponding to the OH group that forms following the cleavage of the side-chains from the aromatic rings. The intense band corresponding to the amide carbonyl at around 1650 cm^{-1} in both spectra shows that the polymer backbone structure is not affected by the transformation procedure. These spectra show that the side-chains may be successfully removed from the polymer chains without affecting the integrity of the rigid-rod structure. This is a reflection of the disparate reactivities of esters and amide functionalities towards basic hydrolysis. The intensities of the i.r. absorption bands may be used to follow the transformation reaction, and the results for a film 1 μm thick are shown in *Figure 3*. These may be fitted to a diffusion-limited process with a diffusion coefficient of 5×10^{-6} μm s^{-1}. Clearly, the diffusion process is slow given the poor solubility of the R100 polymer in water. For the transformation process we do not wish to destroy the film structure and hence a very poor solvent is required. Mixed solvents may enhance the reaction rate by optimizing the diffusion and dissolution for both reactant and products. Transformed films of R100 showed

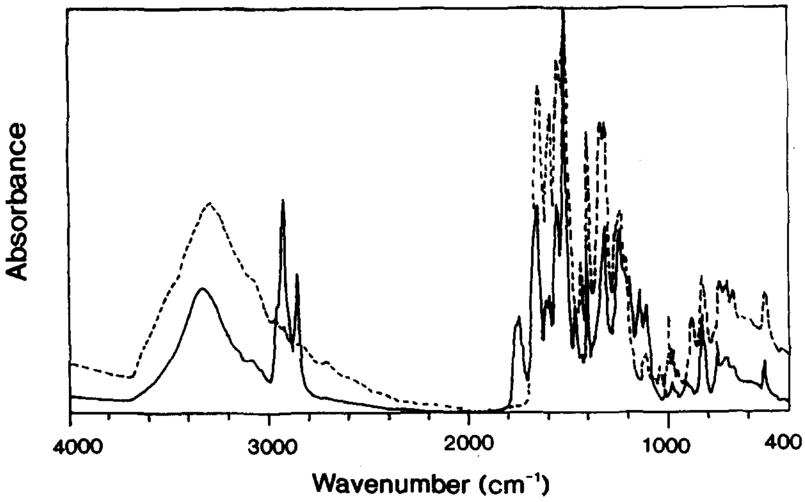


Figure 2 I.r. spectra for thin films of the polymer R100 obtained before transformation (——) and after transformation (---), which leads to the cleavage and removal of the flexible side-chains

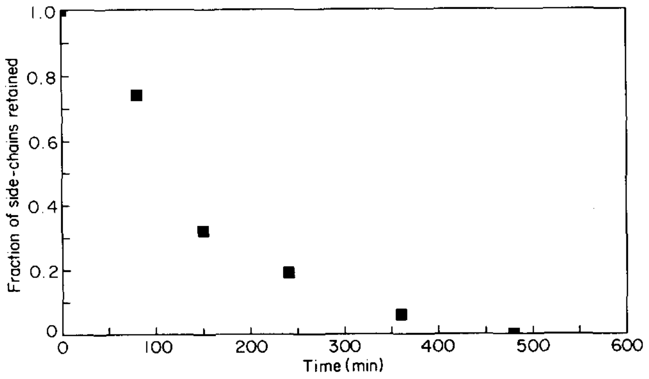


Figure 3 Plot of the fraction of side-chains remaining in thin films of R100 recorded using *FT*i.r. as a function of the transformation time

no solubility in THF, in contrast to the good solubility of the untransformed film, as shown in *Table 2*.

The chemical transformation process leads to a roughening of the initially smooth surface, which could be seen most easily on transformed fibres using scanning electron microscopy. However, a smooth surface could be recovered by heat treatment at 100–150°C.

Summary

We have shown that highly soluble rigid-rod polyamides may be prepared by the addition of substantial alkyl-based side-chains through an ester coupling to the aromatic rings in the main-chain. The excellent solubility in conventional solvents, such as THF, allows thin films and fibres to be prepared. Subsequent to the fabrication process the side-chains can be cleaved from the rigid-rod core and removed from the polymer film. The removal of the side-chains transforms both the chemical structure and the physical properties. Such transformed films are now insoluble in THF. The transformation mechanism is clearly diffusion limited, but there is some scope for optimization of the process through the design of the side-chains and the use of mixed solvent systems.

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