Synthesis and Some Properties of Polyrotaxanes Comprised of Polyurethane Backbone and Crown Ethers

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Rotaxane chemistry provides a new direction of research in polymer architectures. Unlike conventional polymers, polyrotaxanes are molecular composites comprised of macrocycles threaded by linear polymer backbones with no covalent bonds between the two components. Since the first idea of a stable union of a linear molecule threaded through a cyclic one was born in 1961,[1] syntheses of several monomeric and oligomeric rotaxanes have been reported.[2] A special type of polycatenane, which may also be classified as polyrotaxanes with weak cross-linking to prevent dethreading of macrocycles, has also been investigated.[3] However, few data had been obtained on polyrotaxanes until we recently reported the synthesis of several types of polyrotaxanes.[4] We now report the synthesis and some thermal and solution properties of polyurethane rotaxanes based on 60-crown-20 (60C20) and 36-crown-12 (30C10).

As shown in Scheme I, polyrotaxanes 1 and 2 were synthesized via the *statistical threading* method performed by carrying out the polymerization of tetraethylene glycol and methylenedi-*p*-phenyl diisocyanate (MDI) using melted 60C20 and 36C12 as solvents, respectively. The mixtures of tetraethylene glycol and melted crown ethers were stirred for 1 h prior to the polymerization to allow threading between the cyclic and linear species. In order to provide a reference for comparison to the properties of the polyrotaxanes, the corresponding model polymer 3 was prepared under the same conditions except diglyme was used as the solvent instead of a crown ether.

The polyrotaxanes were purified by multiple reprecipitations into solvents in which the polyrotaxane can precipitate but the crown ether is very soluble. Thus, 1 and 2 were reprecipitated into ethyl acetate and methanol, respectively. The reprecipitation was repeated for each polymer until a constant composition (x/n value) was reached.[5] Even though there were no blocking groups at the chain ends, dethreading of the macrocycle was not significant. This probably is due to the random coiling of the chains and attractive intraannular hydrogen bonding between rings and chains in solution and chain entanglements and unfavorable dethreading kinetics in the solid state.

The polyrotaxanes and the model polymer have similar ^{1}H NMR spectra except that (1) 1 shows a larger peak at 3.50 ppm due to the overlap of the singlet 60C20 peak with the one for the ethyleneoxy protons in the polymer backbone and (2) 2 shows an extra singlet 36C12 peak at 3.52 ppm. Integrations of these macrocycle signals (with correction for the ethyleneoxy protons in the polymer backbone) relative to the aromatic protons enable the compositions of the polyrotaxanes to be determined.

The polyrotaxanes and model polymer have comparable molecular weights as determined by GPC. Figure 1 shows GPC traces of the polyrotaxane 2 and a physical blend containing model polymer 3 and 36C12 which was in the same weight percentage as that in the polyrotaxane. It is clear that 36C12 and the polymer backbone can be separated when they were blended, but can not be separated when they formed a polyrotaxane.

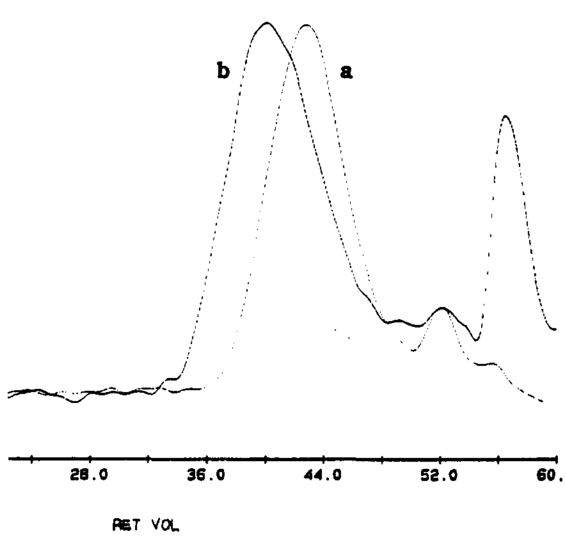
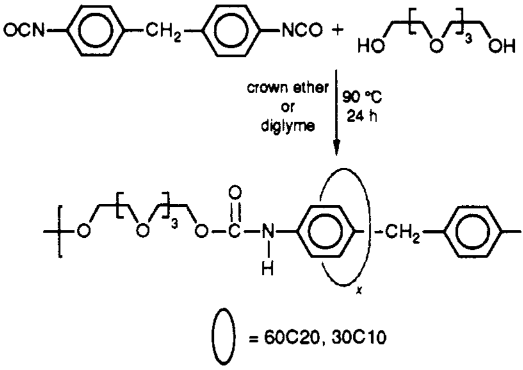


Figure 1. GPC traces (solvent: THF) of (a) polyrotaxane 2 and (b) a physical blend containing model polymer 3 and 36C12 (16 wt %). Molecular weights of the polymers based on polystyrene calibration. 1 (the trace is now shown): $M_n = 7.54 \times 10^3$, $M_w = 13.4 \times 10^3$. 2: $M_n = 7.24 \times 10^3$, $M_2 = 10.8 \times 10^3$. 3: $M_n = 12.0 \times 10^3$, $M_w = 27.0 \times 10^3$.

Scheme I
Syntheses of Polyrotaxanes and the Corresponding Model Polymer



1, polyurethane–rotaxa-60C20 (x/n = 0.57)
2, polyurethane–rotaxa-36C12 (x/n = 0.16)
3, model polyurethane (x/n = 0.00)

The polyrotaxanes are more soluble in common solvents. For example, 3 is insoluble in water, methylene chloride, and acetone, but 1 and 2 are soluble in methylene chloride and acetone; 1 is even soluble in water. Enhancement of the solubilities through rotaxane formation is generally due to the strong interaction between crown ethers and solvents, also reduction of backbone intermolecular interactions.

TGA analysis showed that the model polymer is stable up to 270 °C, but the polyrotaxanes started to lose weight at 175 °C, the onset decomposition temperature of crown ethers. DSC traces of the polymers are shown in Figure 2. As expected, the glass transition temperatures of the polyrotaxanes [−28 °C (1) and +19 °C (2)] are lower than that of the model polymer (+51 °C). The films cast from the polyrotaxanes are rubbery, but the one from the model polymer is rigid. The decrease in the glass transition temperature of the polyrotaxanes results not only from the copolymer effect but also from additional ring effects since the macrocycles are not covalently bonded to chains but

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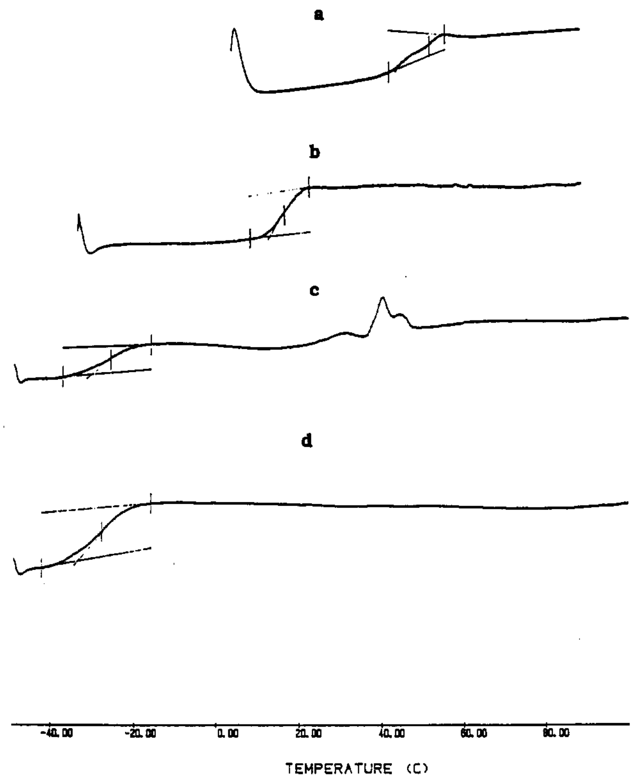

Figure 2. DSC traces of polymers which had been aged for 2 months at room temperature: (a) model polymer 3 (first run); (b) polyrotaxane 2 (first run); (c) polyrotaxane 1 (first run); (d) polyrotaxane 1 (second run).

motionally restricted by threading. The rings are believed to cause loose packing of the macromolecules in the solid state and probably facile intraannular hydrogen bonding between macrocycles and the polymer backbone, resulting in diminution of intermolecular backbone–backbone hydrogen bonding between urethane moieties.

More interestingly, the first run of DSC for 1 right after the polymer was prepared showed no transition at all in the range of 25–185 °C; the same was true for 2. However, the first run on the same sample (1) 2 months later shows a melting transition of 60C20 at 40 °C, which is 18.5 °C lower than that of pure 60C20, indicating that the macrocycle has not dethreaded from the backbone. This melting behavior was absent in the second run done after the sample was naturally cooled down, again indicative of the fact that dethreading had not occurred. The same phenomenon was observed after 6 months when we reran the DSC. Parts b and c of Figure 2 show the DSC traces of the first and second runs 6 months after the sample was prepared. The results reveal that the 60C20 can slowly slip along the chain to form crystalline microphases, driven thermodynamically by formation of the stronger urethane–urethane intermolecular hydrogen bonds and crystallization of the macrocycle. However, this behavior was not observed for 2, which contains the smaller crown ether.

In summary, we have synthesized two novel materials whose properties are derived not directly from covalent bonding but from the physical connection of the components. Relatively high threading efficiencies [57% (1) and 16% (2)] were obtained with this system, probably because of the compatibility of the crown ether and the glycol, and also the larger the crown ether size, the higher the threading efficiency. The polyrotaxanes have significantly lower glass transition temperatures than the model polyurethane. Crystallization occurs in 1 without dethreading of the macrocycle. This phenomenon provides evidence that improved processability and ordering may be possible simultaneously with well-designed polyrotaxanes.

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(5) Monomer feed (crown/glycol) molar ratios were 1.07 (1) and 1.50 (2). The x/n values corresponding to the first through the fourth reprecipitations determined by ^{1}H NMR analyses were 0.90, 0.55, 0.58, and 0.57 (1) and 0.19, 0.15, 0.16, and 0.16 (2).