

Synthesis and Characterization of Rigid Cyclic Oligomer Containing Thioether Moiety

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Abstract:

Base on the technology of modified pseudo-high-dilution, we have synthesized a new rigid cyclic oligomer successfully. The new oligomer was characterized by IR, MALDI-TOF-MS, ¹H-NMR and DSC. At the same time, we have explored the behaviors of ring-opening polymerization and cross-linking preliminarily.

Keywords: rigid cyclic oligomer, ring-opening polymerization, cross-linking.

Introduction

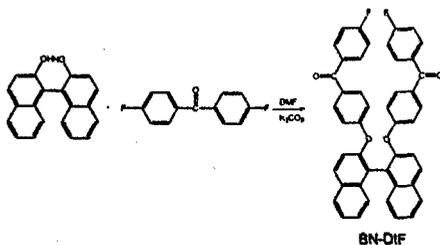
High melt viscosity problem and byproducts often appeared during the course of polymerization. In order to avoid these problems occurring, many researchers have taken the rigid cyclic oligomers as intermediates for the synthesis of high-performance engineering polymers in recent years¹. A series of rigid cyclic oligomers, such as cyclic poly (ether ketone)^{2,3}, cyclic poly (ether sulphone)^{4,5} and cyclic poly (aryl ether ester)^{6,7}, etc. At the same time, many researchers considered introducing the thioether moiety into the fundamental chain of linear polymers to enhance the performance in which sulfur acts as a cross-linking point.

Here we report the synthesis and characterization of rigid cyclic oligomer containing thioether moiety, we have explored the behaviors of the ring-opening polymerization and cross-linking preliminarily. On the other hand, we consider using cyclic cross-linking to realize the polymerization of macrocycle. Through controlling the annealing temperature or time and so on to realize ordered cross-linking.

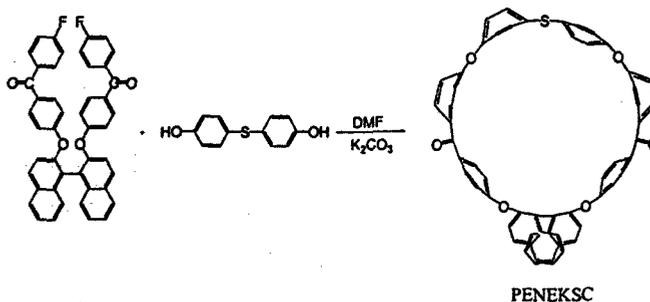
Experimental

Synthesis of BN-DIF. A mixture of DMF (500ml), toluene (80ml), 4,4'-difluorobenzophenone (218g, 1mol) and anhydrous potassium carbonate (14.21g, 0.103mol) was heated to reflux under pure nitrogen with stirring. Then the DMF solution of 1,1'-Bi-2-naphthol (28.63g, 0.1mol) was added for 1h, after the addition, the solution reacted for another 8 hours. The product solution was concentrated and poured into hydrochloric acid (3%, 2000ml), and then a white precipitate was obtained. After the crude product was filtered, washed by distilled water, dried, the crude

product was purified through reduced pressure distillation, and then washed by ethanol for 5 times, upon dried at 60°C under vacuum.



Synthesis of PENEKSC. The macrocyclic oligomer PENEKSC was prepared via aromatic nucleophilic substitution by so-called modified pseudo-high dilution technique. A mixture of DMF (1000ml), toluene (100ml), and anhydrous potassium carbonate (1.66g, 12mmol) was heated to reflux under pure nitrogen with stirring. Then the DMF solution of BN-DIF (2.73g, 4mmol) and 4,4'-Thiodiphenol (0.87g, 4mmol) was slowly added over 14h, after the addition, the solution reacted for another 2 hours. The product solution was cooled and filtered to remove salt. The solution was then concentrated to 25ml and then poured into hydrochloric acid (3%, 2400ml). A white precipitate was obtained and washed with ethanol and water. The crude product was recrystallized twice from acetone and pure product of PENEKSC was obtained.



Results and Discussion

The macrocyclic oligomer PENEKSC was characterized by IR, MALDI-TOF-MS, ¹H-NMR and DSC.

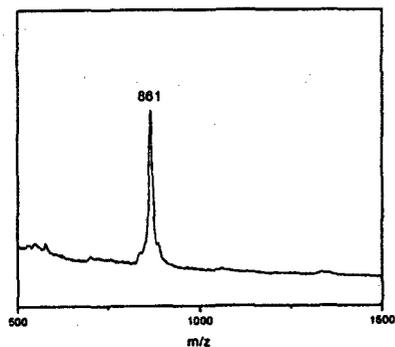
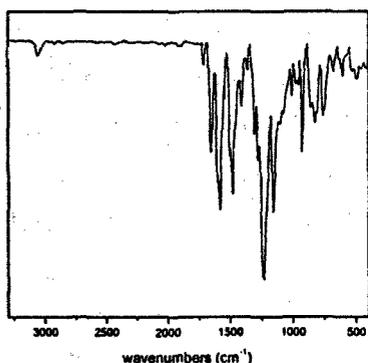


Figure 1. Infrared spectrum of PENEKSC **Figure 2.** MALDI-TOF-MS of PENEKSC

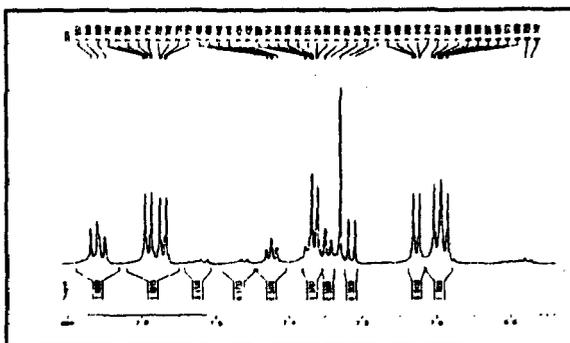


Figure 3. $^1\text{H-NMR}$ spectrum of PENEKSC

Its IR spectrum was shown as Figure 1, from its IR spectrum, we can see the peaks of C=O stretching vibration at 1648 cm^{-1} , -O- stretching vibration at 1233 cm^{-1} , the breathing vibration of benzene at 1480 cm^{-1} and 1582 cm^{-1} , its MALDI-TOF-MS was shown as Figure 2, and its $^1\text{H-NMR}$ spectrum was shown as Figure 3.

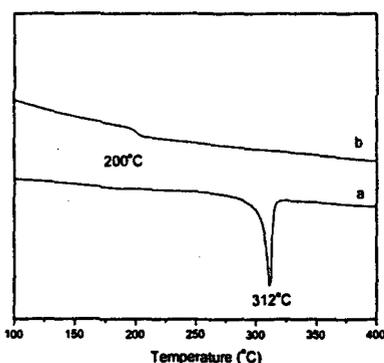


Figure 4. DSC trace of PENEKSC and the product of cross-linking

- (a) Powder sample, (heated from 100°C to 400°C with the rate of 20°C per minute).
- (b) Annealing 5 hours at 380°C , (heated from 100°C to 400°C with the rate of 20°C per minute).

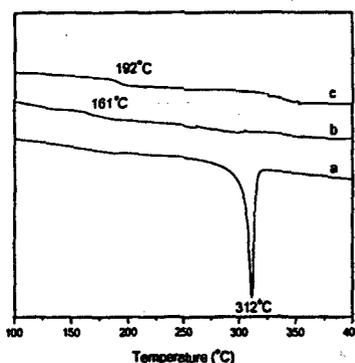


Figure 5. DSC trace of PENEKSC, linear polymer and the product of cross-linking

- (a) Powder sample, (heated from 100°C to 400°C with the rate of 20°C per minute).
- (b) Linear polymer after ring-opening polymerization, (heated from 100°C to 400°C with the rate of 20°C per minute).
- (c) Annealing 5 hours at 380°C , (heated from 100°C to 400°C with the rate of 20°C per minute).

From Figure 4, we can see that the melting point of PENEKSC is 312°C , and after annealing 5 hours, PENEKSC occurred cross-linking partial. The melting point was disappeared and its T_g is 200°C .

From Figure 5, we can see that linear polymer after ring-opening polymerization of PENEKSC is amorphous and its T_g is 161°C, and after annealing 5 hours, the linear polymer occurred cross-linking partial. Here its T_g is 192°C.

Conclusions

We have synthesized rigid cyclic oligomer (PENEKSC) containing thioether moiety successfully. PENEKSC was characterized by IR, MALDI-TOF-MS, ¹H-NMR and DSC. We find that PENEKSC and the linear polymer after ring-opening polymerization can occur cross-linking.

Through controlling annealing temperature or time to realized ordered cross-linking of macrocycle, forming rigid nanotube is expected finally.

Acknowledgements. The financial support of the National Nature Science Foundation of China (NNSFC20104003) is gratefully acknowledged.

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