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Synthesis and Characterization of a Novel Thermo-Sensitive Copolymer of *N*-Isopropylacrylamide and Dibenzo-18-crown-6-diacrylamide

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Experimental Part

Synthesis of the Crown Ether Monomer

The crown ether monomer, which had two polymerizable end groups, was prepared by reacting the corresponding amino crown ether with acryloyl chloride. The reaction path is shown in Scheme S1.

Cis-dinitrodibenzo-18-crown-6 (*cis*-NDBC) was obtained using the method reported by Feigenbaum *et al* [1] and had a melting point (mp) of 207-213 °C (lit. 208-213 °C). *Cis*-diaminodibenzo-18-crown-6 (*cis*-AmDBC) was prepared as describe by Shchori [2] and had a mp of 183-184 °C (lit. 180-184 °C).

Cis-dibenzo-18-crown-6-diacrylamide (*cis*-DBCAm) was synthesized via acylation of

cis-AmDBC with acryloyl chloride. Specifically, 1.0 g of *cis*-AmDBC was dissolved in 15 ml of *N,N*-dimethylformamide (DMF), mixed, and added into a 50 ml round-bottomed flask. 2 ml of triethylamine was added as a hydrogen chloride acceptor. The flask was then placed into an ice bath to keep the temperature of reaction below 3 °C, and the acylation solution (0.6 ml of acryloyl chloride in 5 ml of DMF) was slowly added into the flask. Whereafter the reaction was stirred at room temperature for 3 h. When the reaction was completed, the products were precipitated by adding the solution, which had been filtered to remove the salt, to a mass of ice-water to precipitate the products. The products were dried *in vacuo* at 50 °C for 48 h.

The structure of *cis*-DBCAM was characterized by Fourier transform infrared (FT-IR) spectroscopy in the range of 4000-400 cm^{-1} with an FT-IR Nicolet 560 spectrometer (P-E Com., US) using KBr discs.

Results and Discussion

Characterization of the Crown Ether Monomers

Figure S1 shows the FT-IR spectra of dibenzo-18-crown-6 (DBC) and *cis*-dibenzo-18-crown-6-diacrylamide (*cis*-DBCAM). In the spectrum of *cis*-DBCAM, the peak at 1664.17 cm^{-1} was attributed to the C=C stretching vibration of *cis*-DBCAM propylene group. The peak at 3440.53 cm^{-1} was assigned to the N-H stretching vibration of the acrylamide group. These results indicated that both the modification of DBC and the synthesis of a crown ether monomer with polymerizable end groups were successful.

Characterization of the PNIPAM-co-cis-DBCAM Copolymers and the PNIPAM Homopolymer

The FT-IR spectra of the PNIPAM-*co-cis*-DBCAM copolymer and the PNIPAM homopolymer are shown in Figure S2. A comparative analysis of the FT-IR spectra of the PN homopolymer and PND copolymer confirmed the copolymerization of NIPAM and *cis*-DBCAM. Specifically,

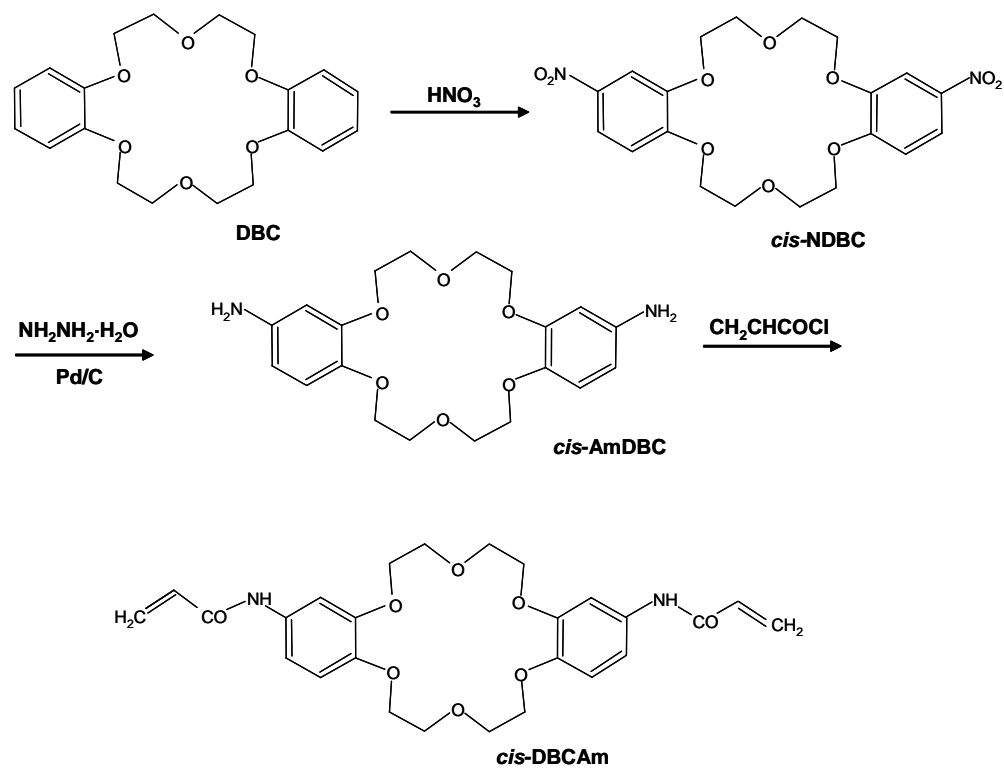
the appearance of the following characteristic bands in FT-IR spectrum of the PND copolymer suggested a successful copolymerization: (1) a strong 1515 cm^{-1} band for C=C skeletal stretching vibration of the phenyl ring, (2) a 1229 cm^{-1} band for C-O asymmetric stretching vibration in Ar-O-R, (3) a 1130 cm^{-1} band for C-O asymmetric stretching vibration in R-O-R', and (4) a 1059 cm^{-1} band for C-O symmetric stretching vibration in Ar-O-R. Corresponding bands also appeared in the FT-IR spectrum of *cis*-DBCAM. These feature peaks suggested the formation of PNIPAM-*co-cis*-DBCAM copolymers.

Effects of the Crown Ether Units on the LCST of Linear Polymers

As shown in Figure S3, when the content of *cis*-DBCAM in the copolymer reached 14.55 mol%, the transmittance change of the copolymer was not sharp enough, and the LCST region was broader. This result indicated that the dramatic phase-transition phenomenon was not very significant when a large amount of hydrophobic comonomer was introduced into the PNIPAM copolymer.

References

- [1] W. M. Feigenbaum, R. H. Michel, *J. Polym. Sci. Pol. Chem.* **1971**, 9, 817.
- [2] E. Shchori, J. Jagur-Grodzinski, M. Shporer, *J. Am. Chem. Soc.* **1973**, 95, 3842.



Scheme S1. Synthetic route of *cis*-dibenzo-18-crown-6-diacrylamide (*cis*-DBCAM).

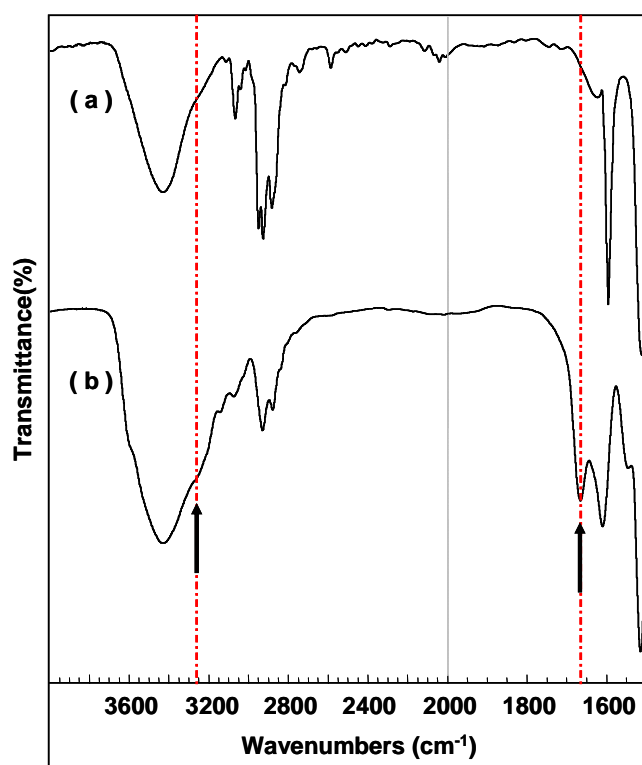


Figure S1. Fragments of the FT-IR spectra of dibenzo-18-crown-6 (a) and *cis*-dibenzo-18-crown-6-diacrylamide (b).

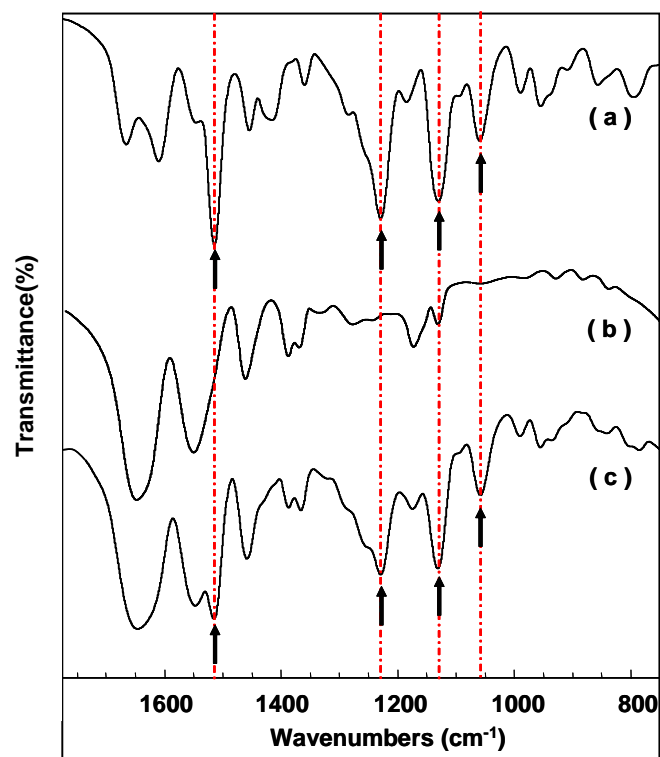


Figure S2. Fragments of the FT-IR spectra of *cis*-DBCAM (a), PNIPAM homopolymer (b) and PNIPAM-*co-cis*-DBCAM copolymer (PND4) (c).

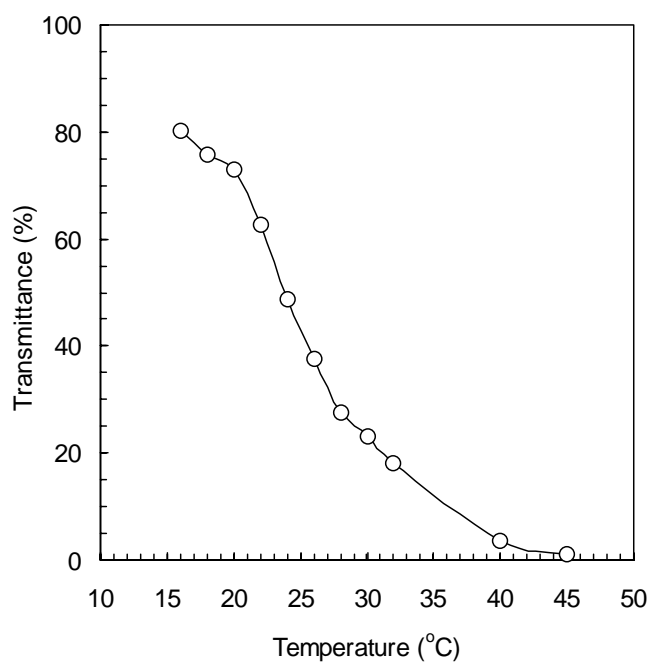


Figure S3. Change in the transmittance of the copolymer in which the molar ratio of *cis*-DBCAm was 14.55 mol%.