Molecular Recognition Directed Phase Transitions in Side-Chain Liquid Crystalline Polymers Containing Crown Ethers

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Both low molar mass[1-10] and polymeric[11-15] liquid crystals containing macroheterocyclic ligands, i.e., azacrowns[2,4-8] and crown ethers,[2,3,12-15] provide a novel approach to self-assembled systems which combine selective recognition with external regulation.[8,9] Only very few preliminary reports on the influence of complexation of low molar mass liquid crystals containing macroheterocyclic ligands and on their phase behavior[3a,b,4c–e,5c] have been reported. It has been already shown that the isotropization transition temperature of low molar mass rodlike liquid crystals containing crown ethers decreases after complexation.[3a,b] A recent publication on disklike crystalline compounds based on an azacrown demonstrated the induction of a mesophase upon complexation.[5c]

Previous publications from our and other laboratories presented the synthesis and characterization of main-chain liquid crystalline polymers containing crown ethers in the main chain[11,12] and of side-chain liquid crystalline polymers containing crown ethers either as part of the mesogenic side group[13,15] or as part of the main chain.[14] The goal of this paper is to report the first series of experiments on the ability to self-regulate the mesomorphic behavior of side-chain liquid crystalline polymers containing crown ethers in the side group via molecular recognition.

Figure 1 outlines the structure of the polymethacrylates 1 and 2 before and after complexation with $NaSO_3CF_3$. The synthesis and characterization of polymers 1 (M_n = 14 600, M_w/M_n = 2.8)[13a,c] and 2 (M_n = 12 200, M_w/M_n = 1.5)[13b] were described in previous publications.

Figure 2a presents the DSC traces[16] of 1 and of some of its complexes with sodium triflate.[17] Polymer 1 was characterized by DSC and X-ray scattering experiments[13a,b] and exhibits enantiotropic nematic (n) and smectic A (s_A) phases. Depending on the kinetic treatment of the sample, the behavior of the s_A phase is more complex. This complex behavior was presented in detail[13c] and is not significant for the present discussion. Figure 2a shows also the DSC traces of the complexes of 1 with 0.3 and 1.2 mol of sodium triflate per monomeric unit or per crown ether. A very clear trend is observed. Upon complexation, the temperature associated with the nematic–isotropic (i) transition increases, while the temperature associated with the s_A–n transition first increases and then decreases, and finally the s_A phase transition disappears. Figure 2b plots the dependences of the glass transition and s_A–n and n–i transition temperatures, as well as of the reverse transition temperatures collected from the cooling scans, as a function of the molar ratio between sodium triflate and structural units. The results from Figure 2b demonstrate that the glass transition and s_A–n and n–i transition temperature first increase. Then the glass transition temperature continues to increase, and the s_A–n transition temperature starts to decrease as the concentration of sodium triflate increases and then disappears, while the n–i transition decreases very little only at high concentrations of sodium triflate. Complexes with higher concentrations of Na/CE than 1.4 were not yet investigated.

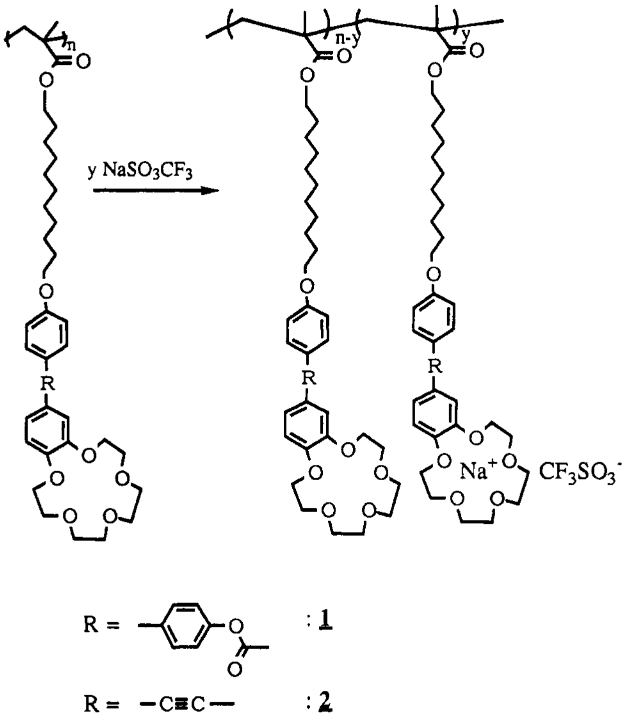

Figure 1. Structure of poly[[[4′-[[[(benzo-15-crown-5)-15-yl]carbonyl]oxy]biphenylyl]oxy]undecan-1-yl methacrylate] poly[[[4-[[(benzo-15-crown-5)-15-yl]ethynyl]phenyl]oxy]undecan-1-yl methacrylate] (2) and of their complexes with sodium triflate.

The phase diagram from Figure 2b resembles that of binary liquid crystalline copolymers generated from two dissimilar structural units, which were extensively investigated in our laboratory.[18] A brief inspection of Figure 1 shows that an oversimplified picture of these complexes resembles that of a copolymer containing complexed and uncomplexed structural units. In fact, due to the cooperative effect of the crown either side groups this picture is more complex, since the ionic interactions between the complexed salt molecules and between the complexed and uncomplexed crown ethers can generate weak physical cross-links.[19] The complexed structural units are more rigid than the uncomplexed ones, and, therefore, the complexed "homopolymer" would exhibit not only both higher isotropization and glass transition temperatures but also a decreased ability to generate higher order smectic and crystalline phases.[20] According to the data from Figure 2b, the complexed and uncomplexed "structural units" of this "copolymer" are isomorphic[21] over their entire range of composition within the nematic phase, but only over a very narrow range of composition within the s_A phase of 1. Accordingly, complexation with more than 0.5 units of sodium triflate per monomeric unit generates a copolymer which exhibits only a broad nematic mesophase.

Figure 2c plots the dependence of the enthalpy change associated with the phase transitions from Figure 2b as a function of the sodium triflate/structural unit molar ratio. The enthalpy change associated with the nematic–isotropic transition decreases with an increase of the concentration of complexed structural units. A qualitative estimation of the nematic–isotropic transition temperature versus copolymer composition according to the temperature transitions and the corresponding enthalpy changes of the two parent homopolymers using the Schroeder–Van Laar equations[18c,22] shows that this dependence would have to

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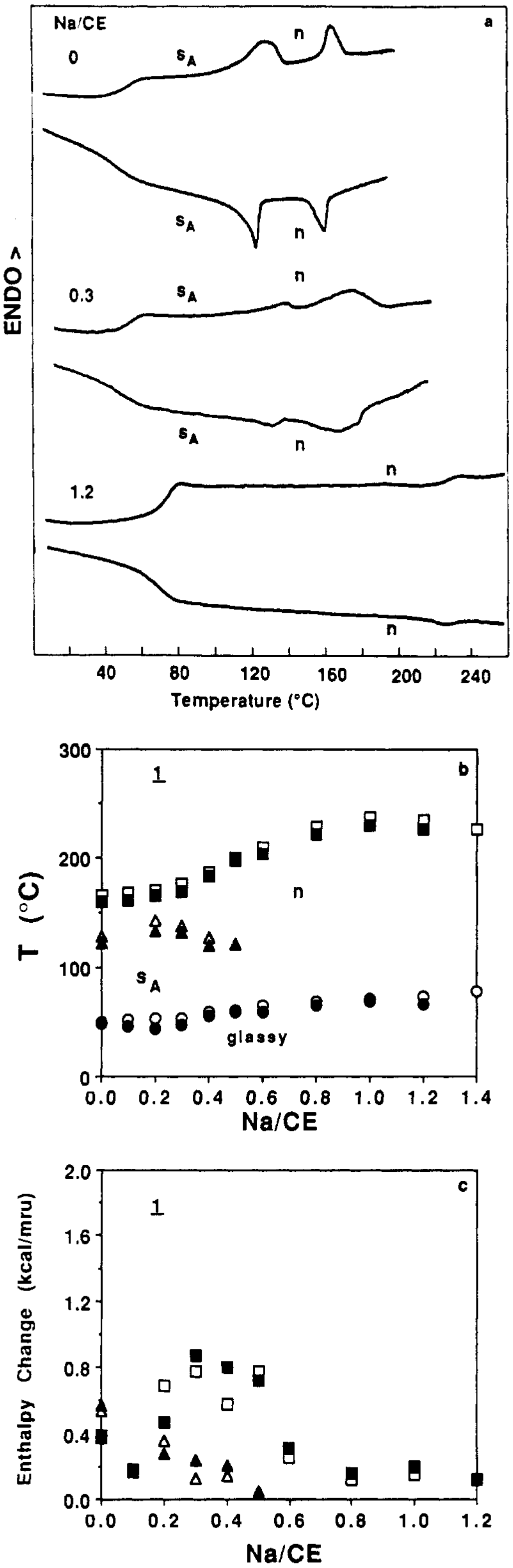

Figure 2. (a) Second heating and first cooling DSC traces (20 °C/min) of 1 (Na/CE = 0) and of its complexes with sodium triflate (Na/CE = 0.3 and 1.2). (b) Dependences of phase transition temperatures of the complexes of 1 with sodium triflate as a function of the Na/CE molar ratio: (○) T_g, (△) s$_A$–n, (□) n–i (data from second heating scan); (●) T_g, (▲) s$_A$–n, (■) n–i (data from first cooling scan). (c) Dependence of the enthalpy changes associated with the phase transitions of the complexes of 1 with sodium triflate as a function of the Na/CE molar ratio: (△) s$_A$–n, (□) n–i (data from second heating scan); (▲) s$_A$–n, (■) n–i (data from first cooling scan).

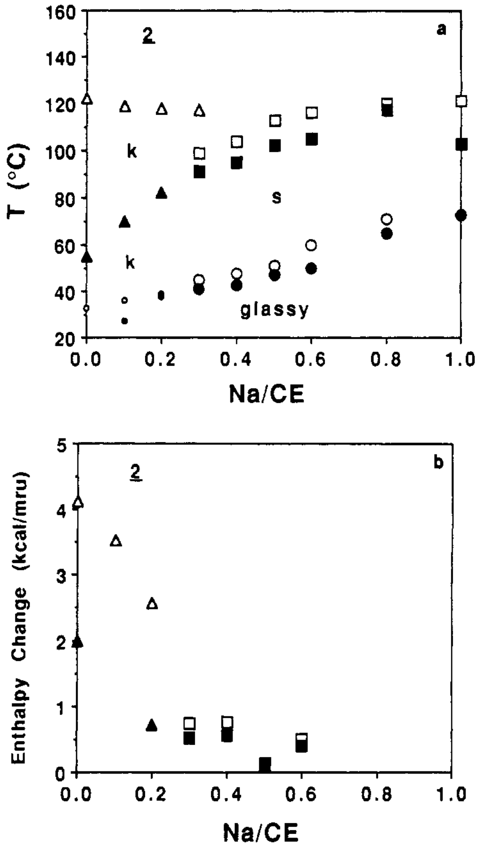

Figure 3. (a) Dependences of phase transition temperatures of the complexes of 2 with sodium triflate as a function of the Na/CE molar ratio: (○) T_g, (△) k–i, (□) s–i (data from second heating scan); (●) T_g, (▲) k–i, (■) s–i (data from first cooling scan). (b) Dependence of the enthalpy changes associated with the phase transitions of the complexes of 2 with sodium triflate as a function of the Na/CE molar ratio: (△) k–i, (□) s–i (data from second heating scan); (▲) k–i, (■) s–i (data from first cooling scan).

exhibit a negative curvature. Therefore, although the two structural units of this copolymer are isomorphic[21] within their nematic phase, they do not behave as an ideal solution.[18c,22] We believe the positive curvature of the dependence from Figure 2b is most probably due to the interaction between the complexed and uncomplexed structural units and/or the ionic interactions between complexed salt molecules.

Polymer 2 is only crystalline;[13b] however, most probably it exhibits a virtual mesophase.[20] Upon complexation with sodium triflate the tendency toward crystallization decreases while the transition temperature associated with the mesophase increases. The entire set of data for the complexes of 2 is plotted in Figure 3a,b. The data from Figure 3a demonstrate the ability to transform the virtual mesophase of 2 into an enantiotropic mesophase via complexation with sodium triflate. According to optical polarized microscopy experiments the enantiotropic mesophase induced via the complexation of 2 with sodium triflate is smectic.

Although a complete characterization and understanding of these systems requires additional experiments, these preliminary results demonstrate the ability to self-regulate the phase behavior of side-chain liquid crystalline polymers containing crown ethers via molecular recognition. In particular, the enhancement of the temperature range of various mesophases via complexation is rewarding. These results provide access to a large variety of fundamental investigations and technological applications.

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References and Notes

(1) Liquid Crystalline Polymers Containing Macroheterocyclic Ligands. 9. Part 8: Reference 13e.

(2) (a) Lehn, J. M.; Malthete, J.; Levelut, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1794. (b) Malthete, J.; Poupinet, D.; Vilanove, R.; Lehn, J. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1016.

(3) (a) He, G. X.; Wada, F.; Kikukawa, K.; Matsuda, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1294. (b) He, G. X.; Wada, F.; Shinkai, S.; Matsuda, T. *J. Org. Chem.* **1990**, *55*, 541. (c) He, G. X.; Wada, F.; Kikukawa, K.; Shinkai, S.; Matsuda, T. *J. Org. Chem.* **1990**, *55*, 548.

(4) (a) Shinkai, S.; He, G. X.; Matsuda, T.; Shimamoto, K.; Nakashima, N.; Manabe, O. *J. Polym. Sci., Part C: Polym. Lett.* **1989**, *27*, 209. (b) Shinkai, S.; Shimamoto, K.; Manabe, O.; Sisido, M. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 361. (c) Shinkai, S.; Nishi, T.; Ikeda, A.; Matsuda, T.; Shimamoto, K.; Manabe, O. *J. Chem. Soc., Chem. Commun.* **1990**, 303. (d) Shinkai, S.; Nishi, T.; Matsuda, T. *Chem. Lett.* **1991**, 437. (e) Nishi, T.; Ikeda, A.; Matsuda, T.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1991**, 339.

(5) (a) Mertesdorf, C.; Ringsdorf, H. *Liq. Cryst.* **1989**, *5*, 1757. (b) Mertesdorf, C.; Ringsdorf, H.; Stumpe, J. *Liq. Cryst.* **1991**, *9*, 337. (c) Liebmann, A.; Mertesdorf, C.; Plesnivy, T.; Ringsdorf, H.; Wendorff, J. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1375.

(6) Lattermann, G. *Liq. Cryst.* **1989**, *6*, 619.

(7) Tatarsky, T.; Banerjee, K.; Ford, W. T. *Chem. Mater.* **1990**, *2*, 138.

(8) Idziak, S. H. J.; Maliszewskyj, N. C.; Heiney, P. A.; McCauley, J. P., Jr.; Sprengeler, P. A.; Smith, A. B., III *J. Am. Chem. Soc.* **1991**, *113*, 7666.

(9) (a) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (b) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.

(10) Vogtle, F.; Knops, P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 958.

(11) Cowie, J. M. G.; Wu, H. H. *Br. Polym. J.* **1988**, *20*, 515.

(12) Percec, V.; Rodenhouse, R. *Macromolecules* **1989**, *22*, 2043.

(13) (a) Percec, V.; Rodenhouse, R. *Macromolecules* **1989**, *22*, 4408. (b) Percec, V.; Rodenhouse, R. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 15. (c) Ungar, G.; Percec, V.; Rodenhouse, R. *Macromolecules* **1991**, *24*, 1996. (d) Rodenhouse, R.; Percec, V. *Makromol. Chem.* **1991**, *192*, 1873. (e) Rodenhouse, R.; Percec, V. *Polym. Bull.* **1991**, *25*, 47.

(14) (a) Rodenhouse, R.; Percec, V.; Feiring, A. E. *J. Polym. Sci., Part C: Polym. Lett.* **1990**, *28*, 345. (b) Percec, V.; Rodenhouse, R. *Adv. Mater.* **1991**, *1*, 1015.

(15) (a) Wen, J. S.; Hsiue, G. H.; Hsu, C. S. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 151. (b) Hsiue, G. H.; Wen, J. S.; Hsu, C. S. *Makromol. Chem.* **1991**, *192*, 2243.

(16) Differential scanning calorimetry (DSC) and optical polarized microscopy experiments (20 °C/min) were performed with the instrumentation and techniques used currently in our laboratory. For experimental details see ref 13a or ref 18a–d. Second and subsequent heating and first and subsequent cooling scans are identical. Therefore, only results obtained from second heating and first cooling scans are reported.

(17) Complexes of 1 and 2 with sodium triflate (T_m = 247–249 °C) were prepared by mixing the solutions of the polymers in dry methylene chloride with the solution of sodium triflate in dry tetrahydrofuran (THF), evaporating the solvent from the resulted solution in a rotary evaporator, and drying the sample in a vacuum oven (60 °C) to constant weight. Transparent solutions were obtained. If the solution of sodium triflate in THF is added to methylene chloride free of polymer 1 or 2, a precipitate results. The absence of the uncomplexed sodium triflate was checked by the absence of its melting endotherm in the DSC scan of the complex.

(18) (a) Percec, V.; Lee, M. *Macromolecules* **1991**, *24*, 4963. (b) Percec, V.; Lee, M. *Polym. Bull.* **1991**, *25*, 131. (c) Percec, V.; Lee, M. *J. Mater. Chem.* **1991**, *1*, 1007. (d) Percec, V.; Zheng, Q.; Lee, M. *J. Mater. Chem.* **1991**, *1*, 1015. (e) Percec, V.; Lee, M. *Polymer* **1991**, *32*, 2862.

(19) For a review on polymers containing macroheterocyclic ligands, see: Smid, J.; Sinta, R. *Top. Curr. Chem.* **1984**, *121*, 105.

(20) For a thermodynamic discussion on the influence of rigidity on crystalline and liquid crystalline phase transitions, see: (a) Percec, V.; Keller, A. *Macromolecules* **1990**, *23*, 4347. (b) Keller, A.; Ungar, G.; Percec, V. In *Advances in Liquid Crystalline Polymers*; Weiss, R. A., Ober, C. K., Eds.; ACS Symposium Series 435; American Chemical Society: Washington, DC, 1990; p 308.

(21) For a discussion on isomorphism of homopolymers and copolymers, both in their liquid crystalline and crystalline phases, see: Percec, V.; Tsuda, Y. *Polymer* **1991**, *32*, 661 and references cited therein.

(22) (a) For a recent discussion on Schroeder–Van Laar equations, see: Van Hecke, G. R. *J. Phys. Chem.* **1979**, *83*, 2344. The simplified version of the Schroeder–Van Laar equation is

$$F_1 = \left\{1 - \frac{\Delta H_1{}^\circ T_2(T - T_1)}{\Delta H_2{}^\circ T_1(T - T_2)}\right\}^{-1}$$

where F_1 is the molar fraction of compound 1 in a binary copolymer or mixture, T_1 and $\Delta H_1{}^\circ$ are its first-order transition temperature and associated enthalpy change, T_2 and $\Delta H_2{}^\circ$ have the same meaning for compound 2, and T is the temperature transition corresponding to F_1. (b) For application of the Schroeder–Van Laar equation to copolymers, see: Achard, M. F.; Mauzac, M.; Richard, M.; Sigaud, M.; Hardouin, F. *Eur. Polym. J.* **1989**, *25*, 593.