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Phase behavior of thermotropic liquid crystalline/conducting polymer blends

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Dedicated to Prof. Dragutin Fleš on the occasion of his 70th birthday

Summary

Liquid crystalline/conducting polymer blends have been prepared. The conductingpolymer [poly(2,5-dimethoxyphenylene vinylene)] retards the liquid crystallinity of the liquid crystalline polymer (hydroxypropyl cellulose), while the liquid crystalline polymer reduces the conductivity of the conducting polymer. However, blends with 17% conducting polymer were both liquid crystalline and conductive.

Introduction

Significant progress continues to be made in the development of electrically conducting polymeric materials suitable for such technological applications as miniature batteries, enclosures for electronic equipment, or field-effect transistors (1-3). The orientation of conducting polymers has proved to be a critical research area as applies to several conducting polymer systems, since conductivity values can be improved dramatically (4). However, despite the ability to orient conducting polymers, many conducting polymers are still difficult to process by conventional techniques.

Previous research has shown that critical properties of conducting polymers (such as conductivity, processability, and mechanical strength) can be improved by blending with thermoplastic insulators (5-7). Although the excellent processing characteristics (e.g. low melt viscosity) of certain thermotropic main chain liquid crystalline polymers are known (8), little has been reported on blends of conducting polymers with thermotropic liquid crystalline polymers introduced as processing aids In principle, liquid crystalline/conducting polymer blends that are immiscible (but compatible) should be relatively easy to process compared to non-liquid crystalline/conducting polymer blends. However, it is not known how the conducting polymer phase composed of rigid rod macromolecules will affect the ability of the liquid crystalline phase to form.

Recently, the preparation of conducting polmer blends composed of a lyotropic liquid crystalline polymer, [poly(*p*-phenylene terephthalamide)], and a conducting polymer, polyaniline, has been reported (9,10). However, the preparation of the conducting fibers was carried out by fiber spinning with solutions that were not concentrated enough to be liquid crystalline. In this paper, we report preliminary results from a study of the phase behavior and conductivity of *thermotropic* (rather than lyotropic) conducting polymer blends.

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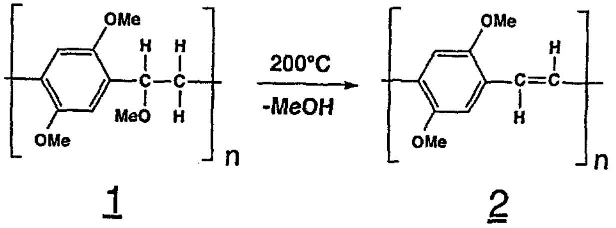
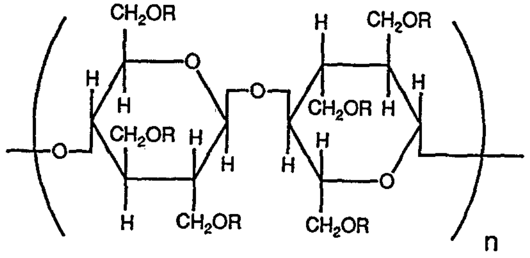
The conducting polymer we have chosen to study is poly(2,5-dimethoxyphenylene vinylene) (DM-PPV, 2) (Scheme I), which is prepared by heat treatment of a thermally unstable precursor polymer 1. Polymer 1 is soluble in common organic

Scheme I



Idealized structure of hydroxypropyl cellulose (HPC)

3



R = $CH_2CHOHCH_3$

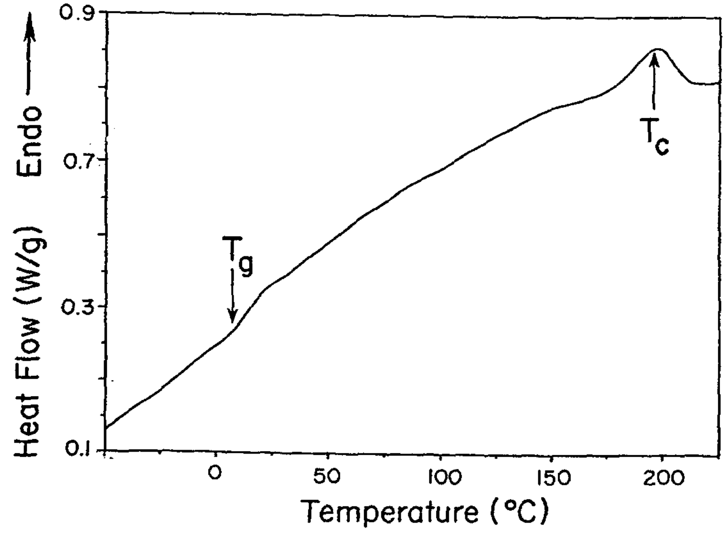


Figure 1. DSC trace of pure hydroxypropyl cellulose (heating cycle)

solvents, and high quality films of 1 can be obtained by solution casting. Polymer 2 conducts electricity when doped with mild oxidizing agents such as iodine, but it is not soluble and does not melt. If polymer 1 is oriented uniaxially during the preliminary stages of the thermal elimination reaction, then the conductivity of 2 in the direction of orientation is improved dramatically (11,12).

The liquid crystalline polymer we have chosen to blend with 2 is a semiflexible derivative of cellulose, hydroxypropyl cellulose (HPC, 3) (13-16). This polymer is both a thermotropic and lyotropic liquid crystalline polymer (forming cholesteric phases) and is soluble in water and common organic solvents. The glass transition temperature (T_g) of 3 is relatively low for a main chain liquid crystalline polymer (15°C), which should facilitate good film formation and a rapid doping process for blends of 2 and 3 (14).

HPC is semicrystalline at room temperature and, upon heating, becomes soft and fluid, due to the formation of a mesophase, at approximately 130°C (14). With further heating, the polymer becomes isotropic at approximately 195°C. As with many main chain liquid crystalline polymers, the liquid crystal-isotropic transition is more reproducible than the crystal-liquid crystal transition. HPC can be spun into fibers from the liquid crystalline melt (17).

Experimental

The precursor polymer 1 was prepared by a literature procedure at Lark Enterprises (Webster, MA) (18). Chloroform solutions of 1 were stored at -25° C to prevent undesired thermal elimination reactions and gelation of the solutions. The concentration of solutions of 1 (0.15% by weight) was determined gravimetrically. Polymer 1 was converted to polymer 2 by heat treatment (200°C) under vacuum (<50 μ) for 4 h. Hydroxypropyl cellulose (MW=10^5, Aldrich) was used as received. This polymer contains, on the average, 3.8 moles of hydroxypropyl groups per mole of repeat unit. The structures of 2 and 3 were confirmed by elemental analysis (Microanalytical Laboratory, University of Massachusetts) and FTIR spectroscopy.

Polymer 3 was dissolved in solutions of 1 to yield transparent, homogeneous solutions. Solvent was allowed to evaporate slowly overnight to yield thin films (50 μ thick) that were partially transparent. Films were cut into rectangular strips with scissors. The films were placed between strips of poly(tetrafluoroethylene) and heated at 200°C under vacuum (<50 μ) for 4 h. Blends were prepared that contained 50, 40, 30, 20, 10, and 1% (by weight) of the precursor polymer 1, which corresponds to 46, 36, 26, 17, 9, and 0.8% conducting polymer after the elimination reaction. The structures of the thermally eliminated blends were confirmed by elemental and FTIR analysis.

Differential scanning calorimetry (DSC) analyses were carried out with a Perkin Elmer DSC7 or a Du Pont DSC 10 at a heating/cooling rate of 20°C/min. Samples (10-20 mg) were first cooled to -100°C, then heated to 230°C, and finally cooled to -100°C. This cycle was repeated at least two times. Calibration was carried out with indium standard. The blends were also viewed with a Zeiss optical microscope equipped with polarizing filters, a Linkam hot stage, and a 35-mm camera. The samples were heated from room temperature to 230°C at 20°C/min and cooled at the same rate to room temperature. This cycle was repeated at least two times.

For conductivity measurements, the films were drawn (5X at 140°C) before the thermal elimination reaction. Doping experiments were carried out by immersion of the oriented films in saturated iodine/heptane solutions (2% by weight) and mild agitation of the solutions on a mechanical shaker. The films were removed from the doping solution, rinsed 3X with heptane, and allowed to air dry. Conductivity was measured immediately with conventional four-point probe techniques. After two days of doping, the conductivity of pure HPC was undetectable, and the conductivity of pure DM-PPV had maximized.

Results and Discussion

Phase Behavior

Due to the extreme rigidity of conducting polymer chains, it was not anticipated that a miscible conducting polymer blend of 2 with a semiflexible polymer such as 3 could be prepared. However, good mechanical adhesion between the two phases of these blends resulted in compatible blends with adequate and reproducible mechanical properties. Although both DSC and optical microscopic analyses showed that these blends were phase separated, the presence of the conducting polymer phase influenced the phase behavior of the liquid crystalline phase.

In the heating cycles of the DSC experiment, the liquid crystal-isotropic clearing transition of pure HPC can be detected clearly and reproducibly as an endothermic peak at about 195°C (3-4 J/g; Figure 1) (19). This clearing transition was also detected in blends that contained 0.8, 9, and 17% conducting polymer, but was not detected in blends that contained 26, 36, or 46% conducting polymer. In addition, the enthalpy of the clearing transition for the blend with 17% conducting polymer was very weak (<0.5 J/g). The enthalpy of the clearing transition for the blends with 9 and 0.8% conducting polymer (2-3 and 1.5-2 J/g, respectively) was more similar to the transition enthalpy for pure HPC. The T_g of pure HPC was measured to be 15°C by DSC analysis (Figure 1), and this glass transition was evident in the blends as well.

The optical microscopic analyses were consistent with the DSC measurements. When viewed without crossed polarizers at room temperature, the blends exhibited two-phase morphology. As shown in Figure 2, the conducting polymer phase was reddish in color (darker), while the HPC phase was yellowish (lighter). The analyses with crossed polarizers at room temperature confirmed the DSC data and showed that the HPC phase was amorphous when 26% or greater of the conducting polymer was present. When 17% or less of the conducting polymer was present, the HPC phase was birefringent. The conducting polymer phase was amorphous for all compositions.

When the samples with birefringent HPC phases were heated, the HPC phase was birefringent up to temperatures of 190°C, when birefringence began to disappear. Significantly, when heated at temperatures greater than 120°C, the samples became very soft and could be sheared easily between the microscope slides. Disclination lines were observed in the birefringent HPC phase between 120° and 190°C, which were assigned to the liquid crystalline state. The birefringence observed for the HPC phase of the blends was similar to the birefringence observed with pure HPC in similar heating and cooling cycles. The blends with an amorphous HPC phase at room temperature did not soften significantly when heated. The ability of the conducting polymer phase to retard the formation of liquid crystallinity in the HPC phase, despite phase separation, is believed to result from the rigid rod character of the conducting polymer chains dispersed throughout the liquid crystal domains.

Conductivity

Percolation theory has been used to predict the onset of conductivity in conducting polymer composites and blends (20,21). Experimental results have shown both sharp and gradual onsets of conductivity with an increase in the amount of the conductive phase. The onset of conductivity, which typically occurs at 10-20% of the conductive phase, is believed to occur with the formation of network structures in the conductive phase. However, it is possible that the network formation necessary for conductivity will retard the formation of extended liquid crystalline domains, and this appears to be true for this liquid crystalline/conducting polymer system.

Iodine doping resulted in conducting polymer blends, and conductivity as a function

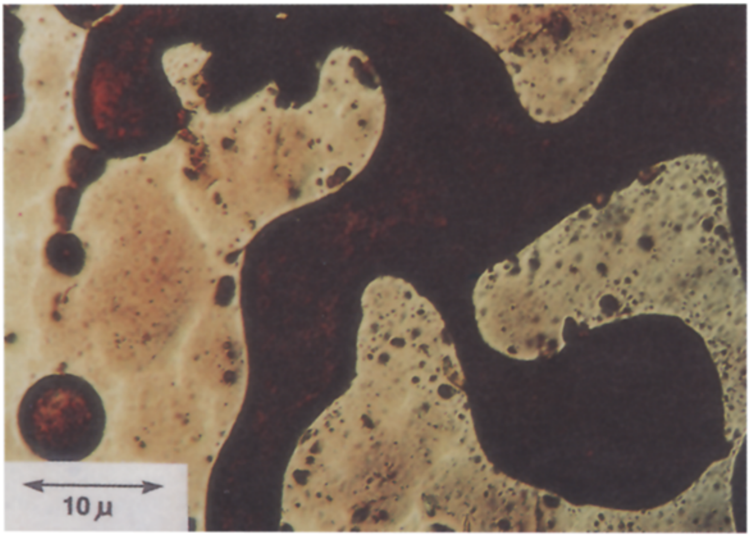


Figure 2. Optical micrograph (without crossed polarizers) for 74/26 HPC/DM-PPV blend.

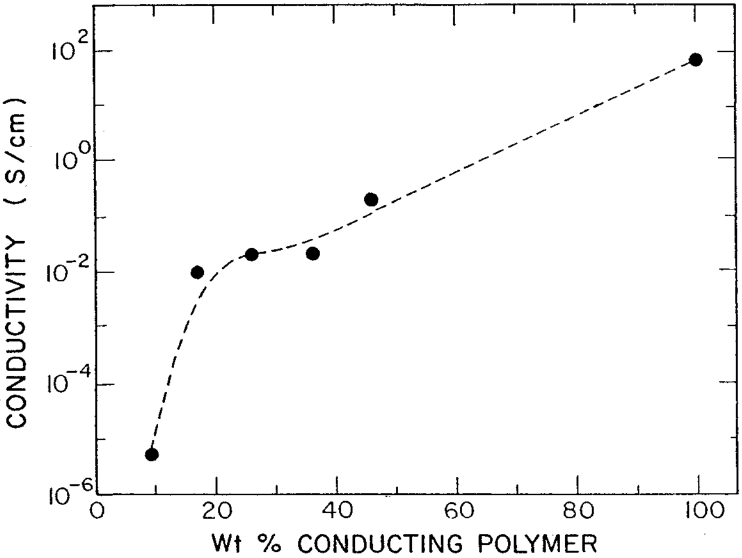


Figure 3. Conductivity as a function of composition.

of blend composition is plotted in Figure 3. The amount of conducting polymer necessary to retard the formation of the liquid crystalline phase (between 17 and 26% by weight) corresponds approximately to the amount of conducting polymer necessary to increase the conductivity from the semiconducting (10^{-6} S/cm) to conducting region (10^{-2} S/cm). It is critical that the blend with 17% conducting polymer is both thermotropic and conducting.

Conclusions

In this study, we have discovered a conducting polymer blend that exhibits thermotropic liquid crystalline behavior. However, the conducting polymer phase retards the ability of the insulating polymer to form the liquid crystalline phase. For the HPC/DM-PPV system, 17% appears to be about the maximum amount of conducting polymer that can be incorporated into the blend, while still retaining the ability to process in the liquid crystalline state. In future work, we will report in more detail the properties of these and other conducting polymer blends.

Acknowledgments

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References

1. Reynolds JR (1988) Chemtech 18: 440
2. Kanatzidis MG (1990) Chem. & Eng. News 68: 36
3. Skotheim TA (ed.) (1986) Handbook of Conductive Polymers I and II. Marcel Dekker, New York
4. Machado JM, Karasz FE, Kovar RF, Burnett JM, Druy MA (1989) New Polym. Mater. 1: 189
5. Machado JM, Karasz FE, Lenz RW, (1988) Polymer 29: 1412
6. Schlenoff JB, Machado JM, Glatkowski PJ, Karasz FE (1988) J. Poly. Sci. Part B: Polym. Phys. 26: 2247
7. Machado JM, Schlenoff JB, Karasz FE (1989) Macromolecules 22: 1964
8. Gordon M (ed.) (1984) Liquid Crystal Polymers I, II, and III (Advances in Polymer Science #59, 60, 61). Springer-Verlag, Berlin
9. Andreatta A, Tokito S, Smith P, Heeger AJ (1990) Mol. Cryst. Liq. Cryst. 189: 169
10. Andreatta A, Heeger AJ, Smith P (1990) Polymer Commun. 31: 275
11. Tokito S, Smith P, Heeger AJ (1991) Polymer 32: 3
12. Gagnon DR, Karasz FE, Thomas EL, Lenz RW (1987) Synth. Met. 20: 85
13. Young RA, Rowell RM (eds.) (1986) Cellulose Structure, Modification, and Hydrolysis. Wiley Interscience, New York
14. Charlet G, Gray DG (1987) Macromolecules 20: 33
15. Samuels RJ (1969) J. Poly.Sci., Part A-2 7: 1197
16. Wang LF, Pearce EM, Kwei TK (1991) Polymer 32: 249
17. Shimamura K, White JL, Fellers JF (1981) J. Appl. Polym. Sci. 26: 2165
18. Tokito S, Momii T, Murata H, Tsutsui T, Saito S (1990) Polymer 31: 1137
19. The melting endotherms for the crystal-liquid crystal transition of pure HPC and the blends were not detected after the first heating cycles of the DSC experiments.
20. Scher H, Zallen RJ (1970) J. Chem. Phys. 53: 3759
21. Seager CH, Pike GE (1974) Phys. Rev. B 10: 1435

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