Macromolecules 1993, 26, 4723–4725

Dilute-Solution Chiral Optical Changes Signal the Thermally Reversible Gelation of Poly(*n*-hexyl isocyanate) in Hydrocarbon Solvents

Mark M. Green,* Chetan A. Khatri, Michael P. Reidy, and Kalle Levon

Department of Chemistry and Herman F. Mark Polymer Research Institute, Polytechnic University, Six Metrotech Center, Brooklyn, New York 11201

Received April 19, 1993
Revised Manuscript Received June 16, 1993

Introduction. Two important issues associated with the formation of thermally reversible gels are the effect on the gel properties of the phase conditions attending the always prerequisite poor solvation state of the polymer and the nature of the reversible cross-link points which anchor the gel network.[1] The gathering of the different detailed answers to these questions for the wide variety of polymers which form these reversible networks may lead to a better understanding of the general principles associated with thermally reversible gelation.[2] We here report the observation of a new thermally reversible gel formed from the wormlike and helical poly(*n*-hexyl isocyanate) (PHIC) in hydrocarbon solvents and chiral optical and ultraviolet spectroscopic changes associated with the aggregation events leading to the gelation. These spectroscopic changes together with the nature of the chain conformation[3] demonstrate the development of an aggregate which reduces the number of kinked helix reversals in the chains.

Results and Discussion. A solution of 5 mg/mL of PHIC of a viscosity-average molecular weight (M_V) of about 300 000 dissolved in *n*-hexane forms a cloudy gel on standing overnight at about −10 °C. The same observation is made in *n*-octane on standing at about 15 °C. Even over long periods of time the gels would not flow by gravity nor could a magnet weighing 520 mg in a 2-mL volume of the gel be moved by gravity or by a similar magnet outside the sealed vial. On warming, although clear liquid was increasingly excluded from both gels above the gelation temperature, the completely clear apparently true solution did not form until 14 °C for *n*-hexane and 50 °C for *n*-octane. For the same rate of warming, these observations were reversible for numerous sol–gel cycles.

Figure 1a shows the ultraviolet spectrum for PHIC in *n*-hexane as a function of temperature. A similar spectral shift takes place for PHIC in *n*-octane solvent. The shift in the spectrum takes place at close to −5 °C for *n*-hexane and 10 °C for *n*-octane as demonstrated by the plots of the extinction coefficients versus temperature for each solvent (Figure 1b). At these spectroscopic concentrations (10^{-4} g/mL) there is no visible scattering or gel formation.

We have similarly studied the temperature-dependent UV spectra of a series of solutions of PHIC in various solvents and discovered similar shifts (as in Figure 1) for solvent: *n*-heptane (−1 °C); 2,3,4-trimethylpentane (−7 °C); 2-methylpentane (−2 °C); 2,2-dimethylhexane (8 °C); 4-methylheptane (13 °C); 2,2-dimethylbutane (12 °C); 2,3-dimethylbutane (−4 °C); 3-methylpentane (−8 °C). In each of the above solvents 5 mg of PHIC dissolved in 1 mL of the solvent forms a thermally reversible gel when stored overnight at −20 °C. Several other solvents listed below showed no shift in the UV spectrum of dissolved PHIC and correspondingly no gel formation under the conditions noted above: 1-chlorobutane; 2-chlorobutane; *cis*-decalin; *trans*-decalin; 1-chlorohexane; 1-chloroheptane.

Random copolymerization of *n*-hexyl isocyanate with very small proportions of optically active isocyanate comonomers has been shown to lead to polyisocyanates with disproportionately large optical activities. Whereas in PHIC the chain consists of an equal number of rapidly interconverting left- and right-handed helical blocks separated by infrequent helix reversals,[3] in optically active copolyisocyanates these helical blocks are unequally populated.[4]

Figure 2 shows the optical activity ($[\alpha]_D$) versus temperature for a copolymer prepared from 99.5% of *n*-hexyl isocyanate and 0.5% of the optically active comonomer (*R*)-2,6-dimethylheptyl isocyanate (1) in *n*-hexane or *n*-octane. While in the high-temperature region the disproportionately high optical activities are consistent with the cooperative mechanism at work here,[4,5] lowering the temperature in both solvents leads to a sudden increase in the optical activity at the same temperatures as the observed shift in the ultraviolet spectra. Moreover, in *n*-hexane where the measurements were made to lower temperature, the $[\alpha]_D$ begins to level off near to −600°, a value characteristic of a chain with a single helical sense.[5] Identical behavior is encountered in these nongelling very dilute solutions for high molecular weight samples of copolyisocyanates containing other proportions of 1.

Measurement of the intrinsic viscosity in *n*-hexane as a function of temperature for a copolymer prepared from 98% of *n*-hexyl isocyanate and 2% of 1 leads to the results in Figure 3 which again shows a discontinuity in the temperature region of the ultraviolet spectral shift and the $[\alpha]_D$ increase reported in Figures 1 and 2.

In all cases the high molecular weight polyisocyanates studied in Figures 1–3 exhibit reproducible gel formation at concentrations of 5 mg/mL in these solvents. In contrast, in the case of a sample of PHIC of a viscosity-average molecular weight (M_V) of 185 000 (intrinsic viscosity (THF) = 8.58 dL g^{-1}, 25 °C), we find in a large number of experiments inconsistent behavior in the UV shift and in the observation of the gel even at lower temperatures than used for the high molecular weight samples.

The results above point to an aggregation with a strong molecular weight dependence but with a remarkably low concentration dependence for the critical temperature which leads to gelation at the higher concentrations, i.e., 0.5 w/v %.

The conformational properties of the polyisocyanates require the optical activity changes to be connected to a reduction in the number of helix reversals.[4,5] This fact must be associated with the chain aggregation indicated by both the cloudiness of the gel and the viscosity changes in more dilute solution. This leads to an intriguing connection if we hypothesize a liquid–liquid phase separation into the isotropic and liquid crystal states in the broad biphasic region of the expected phase diagram for this lyotropic mesogen (PHIC).[6–8] The mobile helix reversals in PHIC, causing a kink of about 130° in the local chain direction,[3] are analogous to the "gauche" state in the persistent-rotational isomeric state mesogenic macromolecule described theoretically by Khokhlov and Semenov.[9] According to their analysis, such states would be reduced in population by their interaction with the liquid crystal director field. In PHIC this reduced population of helix reversals would lead to no optical activity consequences since the left- and right-handed helical states would still be of equal probability. In the copolyisocyanates (Figure 2) this would cause an increase in the proportion of the sequences characterized by the

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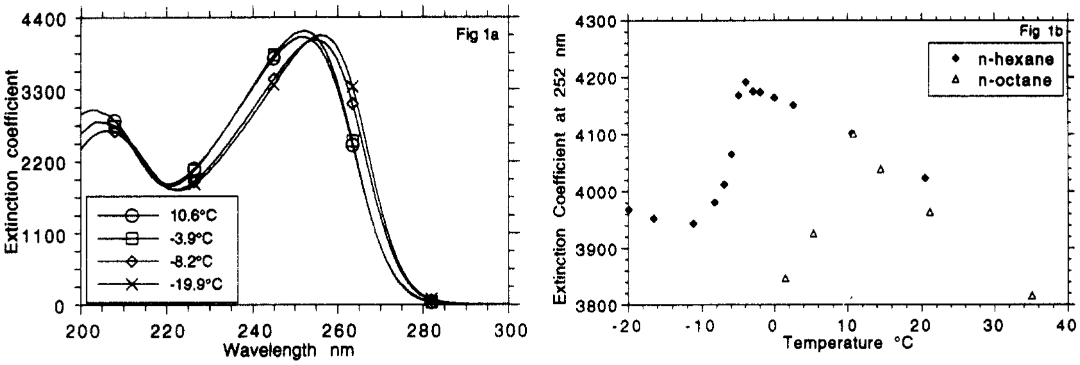

Figure 1. (a) UV spectra for poly(n-hexyl isocyanate) as a function of temperature in n-hexane. (b) Extinction coefficient at 252 nm against temperature in n-hexane and in n-octane.

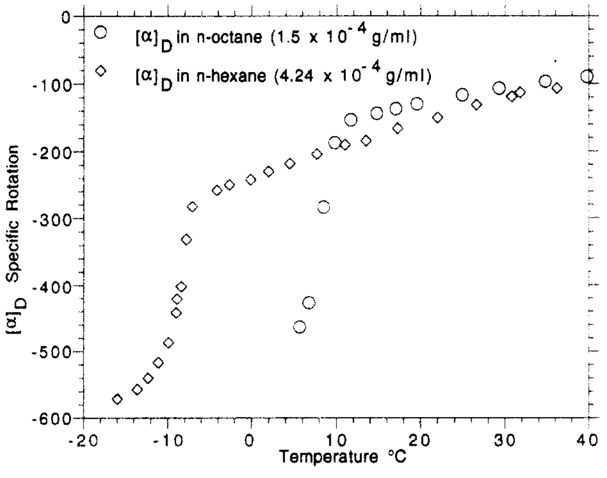

Figure 2. Optical rotation versus temperature for a copolymer of 99.5% n-hexyl isocyanate and 0.5% (R)-2,6-dimethylheptyl isocyanate.

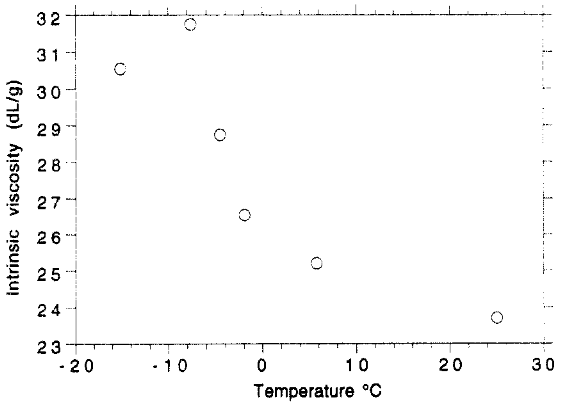

Figure 3. Intrinsic viscosity against temperature for a copolymer of 98% n-hexyl isocyanate and 2% (R)-2,6-dimethylheptyl isocyanate in n-hexane.

lower energy helical sense and therefore a change in the optical activity as observed.

The temperature-dependent circular dichroism spectra in Figure 4 support this aggregate picture since we could therefore expect the chiral optical property to arise from changes in single chains and to vary only in intensity as found.

Empirical force field calculations have shown the helical parameters in poly(alkyl isocyanates) to be easily changed within a wide energy well.[3] Since the ultraviolet spectrum is associated with the backbone chromophore[10] and since the polyamide conjugation in the backbone is sensitive to the twisting about the amide bonds,[3,10] it is reasonable that the UV shifts seen (Figure 1) are associated with small changes in the helix parameters. Such UV changes have been seen as a function of solvent in the polyisocyanates,[10] leading to the reasonable expectation that the solvent exclusion associated with aggregation would lead to changes in the UV spectrum.

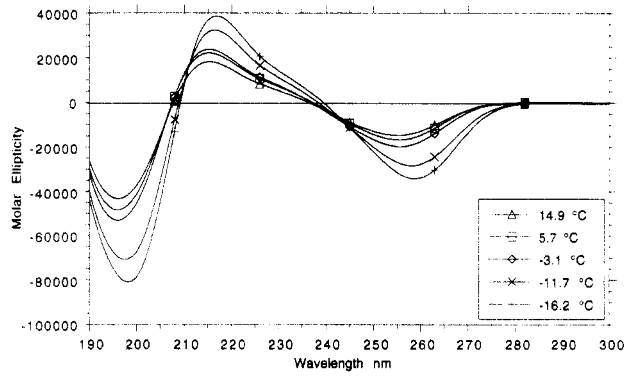

Figure 4. Circular dichroism spectra as a function of temperature for a copolymer of 99% n-hexyl isocyanate and 1% (S)-(2,2-dimethyl-1,3-dioxalan-4-yl)methyl isocyanate in n-hexane.

At this time we have no understanding of the relationships between the various solvents and the spectroscopic/gelation observations although the temperatures associated with the spectroscopic and viscosity changes are linear in the molar volumes of the normal alkane solvents.[11] Although the spectroscopic changes offer insight into the aggregates which anchor the cross-link network, further effort is necessary to determine the phase and morphological characteristics of this new thermally reversible gel.[12,13]

Acknowledgment. We are very grateful to the National Science Foundation Polymers and Chemistry Programs and to the Petroleum Research Fund, administrated by the American Chemical Society, for financial support for this work. We also thank Professor Guy Berry for many helpful discussions. This work is dedicated to our colleague and teacher Professor Herbert Morawetz on his 78th birthday.

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