Macromolecules **2007,** *40,* 661−669

Study of the Microcrystallization of Ethylene−Propylene Random Copolymers in Solution by Fluorescence

Mingzhen Zhang and Jean Duhamel*

Institute for Polymer Research, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Received July 31, 2006; Revised Manuscript Received November 27, 2006

ABSTRACT: The results of fluorescence experiments carried out on two ethylene−propylene copolymers (EP) labeled with pyrene, naphthalene, or both provide the first experimental evidence of intrachain formation of crystalline microdomains in solution. Differential scanning calorimetry (DSC) experiments performed on 50 g/L EP solutions in toluene demonstrated that one EP copolymer was crystalline (EP-CR) while the other was amorphous (EP-NCR). The intrinsic viscosity of EP-CR and EP-NCR in toluene was measured as a function of temperature. EP-CR was the only sample to exhibit a decrease in intrinsic viscosity around 0 °C, suggesting a decrease of the hydrodynamic volume of the polymer coil as expected if EP-CR forms microcrystals in solution. The light scattering intensity of 2 g/L solutions of EP-CR and EP-NCR was also measured as a function of temperature. The EP-CR solutions showed an increase in light scattering intensity at temperatures below 0 °C. The same observations were made with the fluorescently labeled EPs using DSC, intrinsic viscosity, and light scattering measurements, demonstrating that fluorescently labeling the polymers did not affect their solution properties. However, the high sensitivity of fluorescence enabled us to perform experiments at polymer concentrations as low as 20 mg/L. Experiments were carried out using fluorescence resonance energy transfer and pyrene excimer formation that established the absence of intermolecular association at this polymer concentration. These fluorescence experiments indicate that EP-CR undergoes a transition at 0 °C in toluene consistent with a decrease of the hydrodynamic volume of the polymer coil. These experiments constitute the first evidence that crystallization of semicrystalline EPs in solution can occur intramolecularly.

Introduction

It is well-known that for most fluids the viscosity decreases with increasing temperature. For oils, such variations have a negative impact on the normal operation of an automotive engine since the oil cannot properly wet the metal surfaces of the engine if the viscosity is too low. In order to minimize the thinning of the oil that occurs at high temperatures, an oil additive, also called a viscosity index improver (VII), is mixed with the engine oil. The addition of a VII counteracts the reduction in oil viscosity observed at high engine temperatures without excessively increasing the viscosity of the oil at low temperatures.[1−4] Synthetic polymers, such as polymethacrylates,[5] ethylene−propylene random copolymers (EP),[2−4,6] and hydrogenated styrene−diene copolymers,[7] are suited as VII. Owing to the unique polymer coil expansion observed for these polymers with increasing solution temperature, the addition of these polymers to an engine oil helps to offset the detrimental effects of temperature on the engine oil viscosity. As a consequence, the engine oil viscosity remains as constant as possible over the entire temperature range where the engine operates.

One important VII family is that of EPs. EPs with a high ethylene content exhibit long uninterrupted ethylene sequences that crystallize at low temperature and form dense crystalline microdomains. The formation of compact crystalline microdomains at temperatures smaller than the melting temperature T_m results in dense polymer coils. Increasing the temperature above T_m melts the crystalline microdomains, leading to an expansion of the polymer coil. Since the viscosity of the solution is proportional to the fraction of volume occupied by the polymer coils, an expansion of the polymer coil leads to a viscosity increase. Consequently, the ability of EP copolymers to form dense crystalline microdomains at low temperature allows one to use temperature to control the viscosity of the solution.

There are scattered reports in the literature that discuss the solution properties of EP copolymers.[2−4,8−14] Among these, a few have tried to rationalize the effect of temperature on the viscosity of EP solutions.[2−4,12−14] In particular, Rubin et al. observed that the solutions of semicrystalline EP copolymers in toluene were the only ones to exhibit an unusual dependence of the intrinsic viscosity with temperature.[3] They found that the intrinsic viscosity increases rapidly with increasing temperature up to 20 °C, above which it remains constant. They concluded from these observations that the unusual behavior of the solution viscosity exhibited by the semicrystalline EP copolymers in toluene was due to the ability of the EP copolymers to form crystalline microdomains in solution. Dynamic and static light scattering measurements were also performed to demonstrate that semicrystalline EP copolymers undergo unusual conformational changes in tetralin when the temperature was lowered from +50 to −10 °C.[4]

The formation of microcrystals at temperatures lower than T_m implies that polymer−polymer contacts become more favorable than polymer−solvent contacts or that the quality of the solvent toward the polymer decreases. As the polymer becomes less soluble, polymer coils tend to aggregate into large particles which eventually precipitate out of solution. The inherent aggregation of poorly soluble macromolecules often precludes conclusions to be drawn on whether the observed effect for the polymer solution results from the collapse or the aggregation of the polymer coils. Unless specially designed, viscometer or light scattering instruments require solution concentrations in the 1−10 g/L range which are usually too large to prevent aggregation. In order to determine whether the decrease in intrinsic viscosity following the decrease in tem-

10.1021/ma061730f CCC: $37.00

perature of the solution of a semicrystalline EP copolymer is correlated with a collapse of individual polymer coils, this study presents fluorescence experiments on two fluorescently labeled EP copolymers. The highly sensitive fluorescence signal allowed experiments to be performed on solutions containing $0.02-2$ g/L of EP copolymer. The lowest polymer concentrations used with fluorescence were about 2 orders of magnitude lower than those needed by the techniques most commonly used to characterize polymers in solution. Of particular interest for assigning whether the polymers are present as aggregates or individual chains, fluorescence resonance energy transfer (FRET) experiments established that no intermolecular interaction (i.e., aggregation) occurred for polymer concentrations equal to or lower than 0.1 g/L so that the data obtained at these concentrations reflect the behavior of individual polymer coils. This study reports on how fluorescence can be applied in order to monitor the conformation of the coils of individual EP copolymers as they contract while undergoing intramolecular crystallization in solution. It is our hope that such fluorescence-based study can provide an alternative means to characterize the crystallization of polymer chains in solution beside X-ray diffraction, differential scanning calorimetry, and electron microscopy,[15] and more recently atomic force microscopy[16,17] which are traditional tools used in the field.[18]

Experimental Section

Materials. Two EP copolymer samples (EP-CR and EP-NCR) were supplied to us by Imperial Oil (Sarnia, ON). The EP-CR sample exhibits a higher ethylene content toward the middle of the chain. On the other hand, the distribution of ethylene and propylene monomers of EP-NCR is random. The number-average molecular weights of EP-CR and EP-NCR equal 90 and 120 kg mol^{-1}, respectively, with polydispersity around 2.5.

Chemicals and Solvents. Beside the EP copolymers, all chemicals were obtained from Aldrich. High-purity solvents (i.e., distilled in glass or spectrograde) were obtained from EM Science.

Grafting of EP with Maleic Anhydride (MAH). The EP samples were grafted with MAH by following a procedure modified from that reported in ref 19. Briefly, 2.0 g of EP was dissolved in 60.5 g of biphenyl under a nitrogen atmosphere. The mixture was heated to 125 °C under stirring for 5 h until complete dissolution of the polymer. Then 202 mg (1.4 mmol) of *tert*-butyl peroxide radical initiator was added into the reaction flask. The flask was then heated to 170 °C for 15 h, over which 61 mg (0.8 mmol) of maleic anhydride was added stepwisely to minimize the occurrence of cross-linking reactions. The reaction mixture was poured out into acetone to precipitate the grafted polymer. The polymer was dried, dissolved in hexane, and precipitated with acetone. The cycle was repeated four times. Finally, the polymer was dried under vacuum at 50 °C overnight. Since maleation is believed to occur preferentially on tertiary carbons, maleation of EP-CR is more likely to take place at the propylene-richer ends of EP-CR.

Labeling of EP−MAH with a Fluorescent Chromophore. Maleated EP copolymers were labeled with 1-pyrenemethylamine and 1-naphthalenemethylamine according to a procedure described earlier[20] to yield Py-EP and Np-EP, respectively.

Fourier Transform Infrared (FT-IR) Spectroscopy. FT-IR spectra (not shown) were acquired with a MB series Bomem IR spectrophotometer. The presence of MAH attached onto the polymer could be evidenced by the presence of an absorption peak at 1788 cm^{-1} characteristic of the carbonyl groups of succinic andydride. After EP-MAH underwent the labeling reaction, the peak at 1788 cm^{-1} shifted to 1710 cm^{-1}, indicating the presence of succinimide groups, as observed in several other studies from this laboratory.[20−22]

^{13}C NMR Spectroscopy. The spectra of naked EP copolymers were acquired on a Bruker 500 MHz instrument at 300 K. The polymer sample was first dissolved in filtered 1,2,4-trichlorobenzene (TCB) at a concentration of 20 wt %. An antioxidant was added (ca. 0.003 wt %). The solution was then transferred to a 5 mm tube. Analyses were performed with inverse-gated decoupling, a flip angle of 70°, 20 s pulse delay, 5 s acquisition time, and 3000−4000 scans. A ^{13}C NMR spectrum is shown in Figure SI.1 in the Supporting Information (SI).

Table 1. Chromophore Contents of the Labeled EP Copolymers

sample	pyrene content (μmol/g of polymer)	naphthalene content (μmol/g of polymer)
Py-EP-CR	135	0
Py-EP-NCR	129	0
Np-Py-EP-CR	63	91
Np-Py-EP-NCR	59	100
Np-EP-CR	0	158
Np−EP-NCR	0	146

Determination of the Polymer Composition. The composition of the EP copolymers was determined by analyzing the ^{13}C NMR spectra of the naked EP copolymers according to a procedure proposed by Randall.[23] EP-CR and EP-NCR were found to contain 73 and 63 mol % of ethylene, respectively.

X-ray Powder Diffraction. The amorphous or semicrystalline character of respectively EP-NCR and EP-CR was established by X-ray powder diffraction utilizing Cu Kα_1 radiation with an INEL powder diffractometer equipped with a position-sensitive detector. The X-ray diffraction patterns of EP-NCR and EP-CR are shown in Figures SI.2a and SI.2b in the SI.

UV−Vis Absorption Measurements. Absorption spectra were acquired on a Hewlett-Packard 8452A diode array spectrophotometer.

Pyrene (Naphthalene = Np) Content of the Pyrene (Np)-Labeled EP Copolymer. The pyrene content of Py-EP (Np-EP) was determined by measuring the absorption of a dilute solution prepared from a carefully weighed amount, *m*, of pyrene (Np)-labeled polymer in a known volume, *V*, of THF. The pyrene (Np) concentration, [Py] ([Np]), was then estimated from the absorption value at 344 nm (282 nm) and the extinction coefficient of a pyrene (Np) model compound, typically 1-pyrenemethanol or 1-naphthlenemethylamine. Their extinction coefficients were determined in the laboratory and found to equal 42 700 cm^{-1} M^{-1} at 344 nm for 1-pyrenemethanol in THF and 6700 cm^{-1} M^{-1} at 282 nm for 1-naphthlenemethylamine in THF. The pyrene (Np) content, λ, of the polymer could be calculated from $\lambda = [\mathrm{Py}]V/m$ ($[\mathrm{Np}]V/m$) expressed in moles of pyrene (Np) per gram of polymer. The pyrene and naphthalene contents of all polymers used in this study are listed in Table 1.

Pyrene and Naphthalene Content of the Doubly Labeled Copolymers. The pyrene and naphthalene content of the doubly labeled copolymer cannot be obtained in the same manner as done for the singly labeled polymers because the absorption of pyrene overlaps that of naphthalene. First, the pyrene content of the doubly labeled polymer was determined from the pyrene absorption peak at 344 nm which did not overlap the absorption of naphthalene. Second, subtracting the absorption of pyrene from the absorption spectrum of the doubly labeled polymer yielded the absorption spectrum of naphthalene. Third, the naphthalene content of the polymer was then estimated from the absorption peak at 282 nm. This procedure has been described in a previous publication.[20]

Sample Preparation for Fluorescence Measurements. All the labeled EP solutions for fluorescence measurements were degassed under a gentle flow of high purity nitrogen for 20 min. The lowest chromophore concentrations used in this study were 2.5×10^{-6} and 1.5×10^{-5} M for pyrene and naphthalene, respectively, corresponding to polymer concentrations of 0.02 and 0.1 g/L. These concentrations were sufficiently low to avoid the inner-filter effect.[24]

Instrumentation. Steady-state fluorescence emission spectra were acquired on a Photon Technology International LS-100 steady-state system with a pulsed xenon flash lamp as the light source. The solutions containing pyrene or naphthalene were excited at 346 or 300 nm, respectively. The measurements were carried out at various temperatures using a cryostat from Oxford Instruments (Optistat DN) mounted onto the steady-state fluorometer, which allows temperature control within ±0.1 °C. After the set temperature of the cryostat had been reached, the solution was left in the cryostat for 15 min before any fluorescence spectrum was acquired.

DSC measurements were performed on a TA Q100 calorimeter (TA Instruments) calibrated with indium ($T_m = 156.61$ °C). Samples containing ~10 mg of material were weighed and sealed in crimped aluminum pans prior to analysis. An empty aluminum pan was used as the reference, and the chamber was purged with nitrogen during analysis. The temperature of each sample was ramped in two successive steps: (1) for solid-state measurement: heating from −20 to +200 °C followed by cooling from +200 to −20 °C; (2) for solution measurement: heating from −60 to +90 °C followed by cooling from +90 to −60 °C. The sample was allowed to equilibrate isothermally for 5 min between each temperature ramp. The data presented herein are those that were acquired upon cooling the sample with a temperature scanning rate of −10 °C/min to ensure that the measurements were not biased by the thermal history of the sample.

Stability of Polymer Solution at Lower Temperatures. All the results presented in this work were obtained under conditions where the solutions were stable. The experimental protocol used to establish the stability of the solutions is described in the Supporting Information.

Results and Discussion

All experiments presented in this study were performed in toluene. Toluene was selected because it is a nonpolar solvent which has been shown to solubilize efficiently the polar succinimide pendants that were used to connect the chromophores to the EP backbone.[22] In apolar solvents like hexane, the polar succinimide pendants associate leading to the formation of chromophore aggregates which complicate the interpretation of the trends obtained by fluorescence.[20] Using toluene prevented chromophore aggregation and simplified the analysis of the fluorescence data. The high sensitivity of fluorescence enabled the study of polymer solutions at concentration low enough to ensure that information on single polymer coils could be retrieved. Furthermore, the effect of coil contraction following the formation of crystalline microdomains at low temperature has been reported in toluene for EP copolymers.[3]

All experiments were conducted on cooling the samples. Because the rates at which the samples were cooled varied depending on the type of measurement being done (DSC, intrinsic viscosity, light scattering, fluorescence), discrepancies for the onset of crystallization were observed depending on the technique being utilized. For instance, DSC experiments were conducted with a heating/cooling rate of 10 °C/min whereas for all other experiments, the solution was cooled to a set temperature at a rate which depended on either the water bath for the intrinsic viscosity measurements or the cryostat for the light scattering and fluorescence measurements. The solution was then maintained at this temperature for a minimum of 15 min to ensure equilibration before a measurement would be conducted. As pointed out by an unknown referee, differences in the rate of cooling applied by the different instruments used in this study led to some discrepancies for the temperature at the onset of crystallization due to the strong dependence of the rates of nucleation and growth of crystalline microdomains on the rate of cooling.

DSC Measurements. DSC measurements were carried out for the two naked EP samples in the solid state at a heating/cooling rate of 10 °C/min. As shown in Figure SI.5 in the Supporting Information (SI), a peak around 25 °C was observed for EP-CR while no transition peak was observed for EP-NCR. According to the *Encyclopedia of Polymer Science and Engineering*,[25] the glass transition of EP copolymers typically occurs below −30 °C depending on the ethylene content. Therefore, the exothermal peak observed for EP-CR at 25 °C is likely associated with the crystallization of polyethylene stretches in EP-CR taking place in the bulk. This result clearly demonstrates that in the naked form EP-CR is semicrystalline whereas EP-NCR is amorphous.

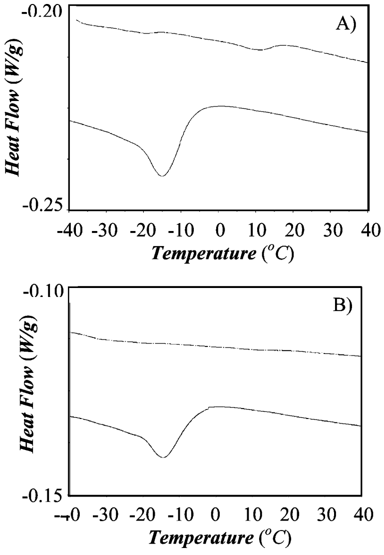

Figure 1. (A) DSC traces of EP-NCR (top) and EP-CR (bottom) in the naked form in toluene ([polymer] = 50 g/L). (B) DSC traces for Py-EP-NCR (top) and Py-EP-CR (bottom) in toluene ([polymer] = 50 g/L). The DSC traces are acquired upon cooling the solution. A decrease in the heat flow indicates an exothermic process.

Since the EP copolymers were labeled with fluorescent probes to perform the subsequent fluorescence experiments, it was required to check whether the introduction of the fluorescent probes onto the EP backbone would affect the crystallinity of the two EP samples. Taking into account that all the subsequent techniques used in this study such as intrinsic viscosity, fluorescence, and light scattering were applied to solutions in toluene, DSC measurements were carried out on toluene solutions containing 50 g/L of the two EP samples in the naked and labeled forms. Figure 1A represents the DSC traces for the naked EPs in toluene. An exothermal peak around −15 °C was observed for EP-CR whereas no peak was found for EP-NCR. The crystallization temperature for the naked EP-CR in toluene is lower than that of the solid-state bulk sample, indicating that the crystalline microdomains of EP-CR are less stable in solution than in the bulk. This observation is in agreement with others made with isotactic polystyrene that show that the melting of polymer crystallites occurred at a lower temperature in solution than in the bulk.[26]

Similar measurements were performed for the pyrene-labeled EPs in toluene. Py-EP-CR and Py-EP-NCR exhibited different DSC profiles shown in Figure 1B. An exothermic peak around −15 °C was observed for Py-EP-CR while no peak was obtained for Py-EP-NCR. Interestingly, the DSC profiles of the pyrene-labeled EPs were identical to those of the unlabeled EPs, indicating that the introduction of the fluorescent probe had little to no effect on the presence or absence of microcrystals in the EP solutions.

The DSC measurements demonstrate that Py-EP-CR forms crystalline microdomains in toluene, but since these experiments were performed in solution at a polymer concentration of 50 g/L, they do not provide information about whether the crystallization occurs intra- or intermolecularly. Indeed a concentration of 50 g/L is 3−5 times larger than the overlap

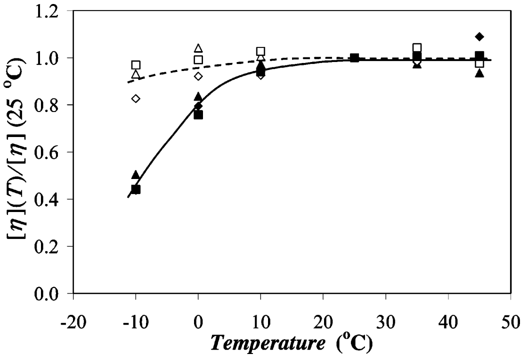

Figure 2. Intrinsic viscosity of EP-CR (filled) and EP-NCR (hollow) in different forms (diamonds, naked; triangles, grafted; squares, labeled) at various temperatures (normalized at 25 °C).

concentration of the EP samples estimated by taking the inverse of the intrinsic viscosity[27] determined in the following section. At such high polymer concentration, it is conceivable that mixed microcrystals are formed involving different chains.

Intrinsic Viscosity Measurements. Viscosity measurements were carried out between −10 and +45 °C for both EPs in the naked, grafted, and labeled forms. The values of the intrinsic viscosity, $[\eta]$, measured for all EP samples are reported in Table SI.1 in the SI. Measurements performed by gel permeation chromatography showed that the molecular weight distribution of the EP copolymers broadens after the grafting and labeling reactions (data not shown). Consequently, $[\eta]$ is expected to vary from sample to sample due to these alterations of the molecular weight distribution. In order to compare the trends obtained with $[\eta]$ as a function of temperature, the intrinsic viscosity values of all EP samples were normalized to their value at 25 °C, and the $[\eta]_T/[\eta]_{25°C}$ ratios were plotted as a function of temperature in Figure 2. Within experimental error, the $[\eta]_T/[\eta]_{25°C}$ ratio remained constant from −10 to 45 °C for the naked, the grafted, and the fluorescently labeled EP-NCR. A different behavior was observed for the EP-CR samples. The normalized $[\eta]$ remained constant between 10 and 45 °C before decreasing continuously with decreasing temperature when the temperature dropped below 0 °C.

Similar trends have been reported in the literature where $[\eta]$ of crystalline polyolefins was found to decrease with decreasing temperature whereas $[\eta]$ of noncrystalline polyolefins remained constant with temperature.[3] Because $[\eta]$ is proportional to the hydrodynamic volume of the polymer coil, V_h, the decrease of $[\eta]$ occurring with decreasing temperatures was interpreted as resulting from a decrease of V_h due to the formation of crystalline microdomains inside the polymer coil. The results shown in Figure 2 indicate that the same effect is taking place with the EP-CR sample. Interestingly, $[\eta]$ in Figure 2 begins to decrease at 0 °C, whereas the DSC results in Figure 1 indicate that crystalline microdomains begin to form between 0 and −5 °C. The correlation observed between the $[\eta]$ trends and the DSC traces supports the explanation that the decrease in $[\eta]$ for EP-CR is due to the formation of crystalline microdomains in the polymer coil. More importantly, the grafting and labeling of the EP samples do not seem to affect their behavior in solution since identical trends of the $[\eta]_T/[\eta]_{25°C}$ ratios are obtained with the EP-NCR and EP-CR samples.

Light Scattering Measurements. Light scattering is a useful method to probe changes in polymer chain conformation or coil size. Light scattering measurements were carried out by using the steady-state fluorometer to irradiate the solution at 500 nm where the chromophores pyrene and naphthalene do not absorb. The light scattering intensity was collected between 497 and 503 nm. All the measurements were acquired with a square quartz cell in the right angle configuration. The temperature-dependent light scattering measurements were also performed for toluene as a control. The labeled and unlabeled EP samples were investigated at a concentration of 2 g/L, the fluorometer used being not sensitive enough to detect scattered light at lower polymer concentrations. The peak intensity at 500 nm was recorded and is plotted in Figure 3 as a function of temperature.

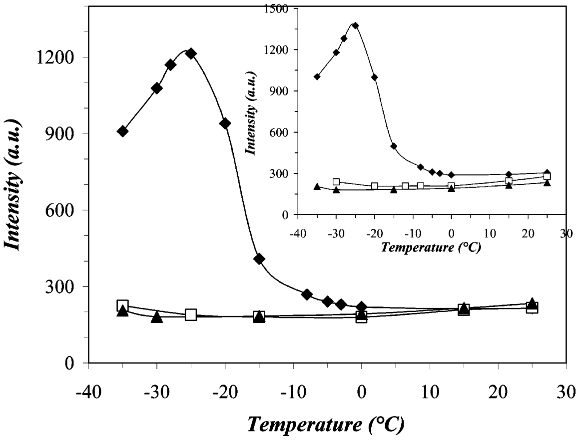

Figure 3. Light scattering measurements of Np-Py-EPs in toluene (diamonds, EP-CR; squares, EP-NCR; triangles, toluene) ([polymer] = 2 g/L, λ_{ex} = 500 nm). Inset shows the light scattering traces of the naked EPs in toluene.

Figure 3 shows that the intensities for toluene and the labeled and unlabeled EP-NCR samples remain relatively constant over the full temperature range. In contrast, the labeled and unlabeled EP-CR samples exhibit a very different intensity vs temperature profile. The intensity remains constant between 0 and 25 °C. When the temperature is decreased below 0 °C, the scattering intensity increases gradually with decreasing temperature, followed by a steep increase at −15 °C until it reaches its maximum value at around −25 °C. Below −25 °C, the intensity decreases with decreasing temperature.

It is interesting that the light scattering increase of EP-CR that occurs at 0 °C in Figure 3 matches the drop in heat flow observed in Figure 1 by DSC. It suggests that increased light scattering is associated with the formation of microcrystals. Semicrystalline polymers like high-density polyethylene or polypropylene appear opaque in the bulk while amorphous polymers are transparent. This behavior is due to the presence of crystalline microdomains in the crystalline polymers which scatter light more strongly than the amorphous polymers, which do not form crystalline microdomains. Figure 3 suggests that the same effect is taking place in solution for the naked and labeled EP-CR (cf. Figure 3 and its inset). As shown by DSC, intrinsic viscosity, and now light scattering, the labeling of the EP samples does not affect the physical properties of the polymers in toluene.

The drop in light scattering intensity observed at temperatures below −25 °C for the EP-CR solution might be due to the precipitation of aggregated EP-CR molecules. This conclusion is supported by the fluorescence experiments reported in Figure SI.3B, which indicated that a 2 g/L EP-CR solution is not stable at −30 °C.

All the experiments carried out so far used polymer concentrations of 50 g/L for DSC, in the 1−4 g/L range for intrinsic viscosity, and 2 g/L for light scattering. Such concentrations are either close to or larger than the overlap concentration, C^*, of the polymers ranging from 6 to 22 g/L depending on temperature and polymer type. The C^* values were estimated

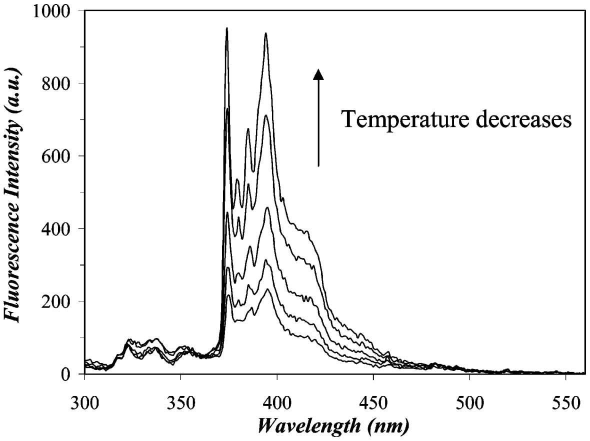

Figure 4. FRET of Np-Py-EP-CR vs temperature (solvent: toluene; $\lambda_{ex} = 300$ nm, [polymer] = 0.1 g/L).

from taking the inverse of the $[\eta]$ values listed in Table SI.1.[27] Consequently, the effects observed in Figures 1−3 could be induced by polymer concentration. To determine whether the crystalline microdomains observed by DSC are generated inside a single polymer coil, one needs to apply a technique which provides information about the polymer coil volume at polymer concentration at least 1 order of magnitude lower than C^*. To this effect, the polymers were labeled with fluorescent chromophores, and fluorescence experiments were performed at polymer concentrations as low as 0.02 g/L, i.e., more than 2 orders of magnitude lower than C^*. The two types of fluorescence experiments that were performed looked, first, at the fluorescence resonance energy transfer (FRET) taking place between an excited naphthalene and a ground-state pyrene and, second, at the formation of excimer between two pyrene labels.

Fluorescence Resonance Energy Transfer (FRET). The grafted EPs were labeled with 1-naphthalenemethylamine and 1-pyrenemethylamine which act as the FRET donor and acceptor, respectively. Although naphthalene exhibits an absorption peak maximum around 278 nm, an excitation wavelength of 300 nm was chosen in order to minimize the emission of toluene which absorbs around 280 nm. The FRET experiments were carried out for the doubly labeled EPs (Np-Py-EPs) in toluene between −35 and 25 °C. The polymer concentration was 0.1 g/L, corresponding to a naphthalene optical density around 0.1 at 300 nm. The fluorescence intensity of the naphthalene monomer, I_{Np}, was calculated by taking the integral of the naphthalene emission intensity between 320 and 326 nm while that of the pyrene monomer, I_{Py}, was obtained from the integral of the pyrene emission intensity between 372 and 378 nm. The I_{Py}/I_{Np} ratio characterizes qualitatively the extent of FRET taking place between naphthalene and pyrene. Higher I_{Py}/I_{Np} values indicate a stronger FRET efficiency.

As shown in Figure 4, the emission profiles characteristic of both naphthalene and pyrene were obtained when Np-Py-EP was selectively excited at 300 nm. The pyrene emission intensity increases with decreasing temperature whereas the naphthalene emission intensity decreases with decreasing temperature. As a consequence, the I_{Py}/I_{Np} value increases with decreasing temperature, indicating that FRET becomes stronger at low temperatures. In order to retrieve quantitative information, the I_{Py}/I_{Np} values were calculated and normalized at 25 °C for both Np-Py-EPs. The normalized I_{Py}/I_{Np} values are plotted in Figure 5 as a function of temperature. Both EPs exhibit similar normalized I_{Py}/I_{Np} ratios between 0 and 25 °C. For temperatures below 0 °C, the I_{Py}/I_{Np} ratio of EP-CR increases much more steeply with decreasing temperature than that of EP-NCR.

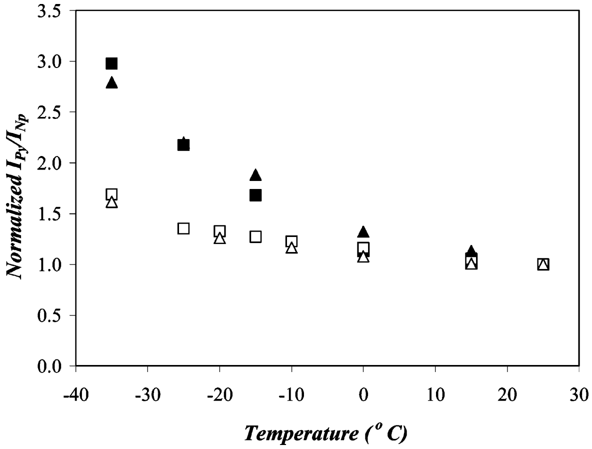

Figure 5. Normalized I_{Py}/I_{Np} for doubly labeled EPs as a function of temperature: EP-CR (filled) and EP-NCR (hollow), [polymer] = 0.1 g/L (squares) and 2 g/L (triangles) (solvent: toluene; $\lambda_{ex} = 300$ nm).

The trends observed in Figure 5 for the I_{Py}/I_{Np} ratio can be easily rationalized by evoking the formation of crystalline microdomains inside the polymer coil. In the course of the microcrystallization of EP-CR, the polymer coil contracts, leading to a smaller average distance spanning the donor naphthalene and the acceptor pyrene. As a result, FRET is enhanced and the I_{Py}/I_{Np} ratio increases. In contrast, since no microcrystallization occurs for the amorphous EP-NCR, the polymer coil contracts less than that of EP-CR. The moderate increase in I_{Py}/I_{Np} observed for EP-NCR at low temperatures might be due to poorer polymer−solvent interactions which could induce a contraction of the polymer coil.

Intramolecular vs Intermolecular Interactions. The FRET experiments performed in Figure 4 were obtained with a polymer concentration of 0.1 g/L, more than 1 order of magnitude smaller than C^* (see Table SI.1). However, even at such low polymer concentrations, intermolecular associations between the chains of modified polymers can still occur via specific interactions.[28] To ensure that this was not the case, FRET experiments were performed on EP solutions, where the same EP sample was fully labeled with either pyrene (Py-EP) or naphthalene (Np-EP). The solutions were prepared with pyrene and naphthalene concentrations of 2.2×10^{-6} and 1.8×10^{-5} M, respectively, which correspond to an overall EP concentration of 0.1 g/L. For each EP sample, emission spectra were acquired at various temperatures for solutions containing Py-EP alone, Np-EP alone, and a mixture of the two. Then the fluorescence spectra of Py-EP alone and Np-EP alone were summed and compared to the fluorescence spectrum of the mixture. The results of this comparison are shown in Figure 6. The perfect overlap observed between the spectra demonstrates that no intermolecular FRET occurs at a polymer concentration of 0.1 g/L. Thus, the trends shown in Figure 5 obtained with a polymer concentration of 0.1 g/L are due to a phenomenon which occurs intramolecularly.

In order to relate the FRET experiments obtained at 0.1 g/L with those obtained by intrinsic viscosity in Figure 2 in a concentration range of 1−4 g/L or light scattering in Figure 3 at 2 g/L, the FRET experiments were repeated with the doubly labeled polymers at a polymer concentration of 2 g/L. Since the chromophore concentration was higher, the overall absorbance of the solution was much larger than 0.1, and the fluorescence emitted by the naphthalene was absorbed and reemitted by the pyrene labels, a phenomenon which can be referred to as direct energy transfer (DET). As a result, DET enhanced the I_{Py}/I_{Np} ratios obtained at polymer concentrations of 2 g/L compared to those obtained at 0.1 g/L. Nevertheless,

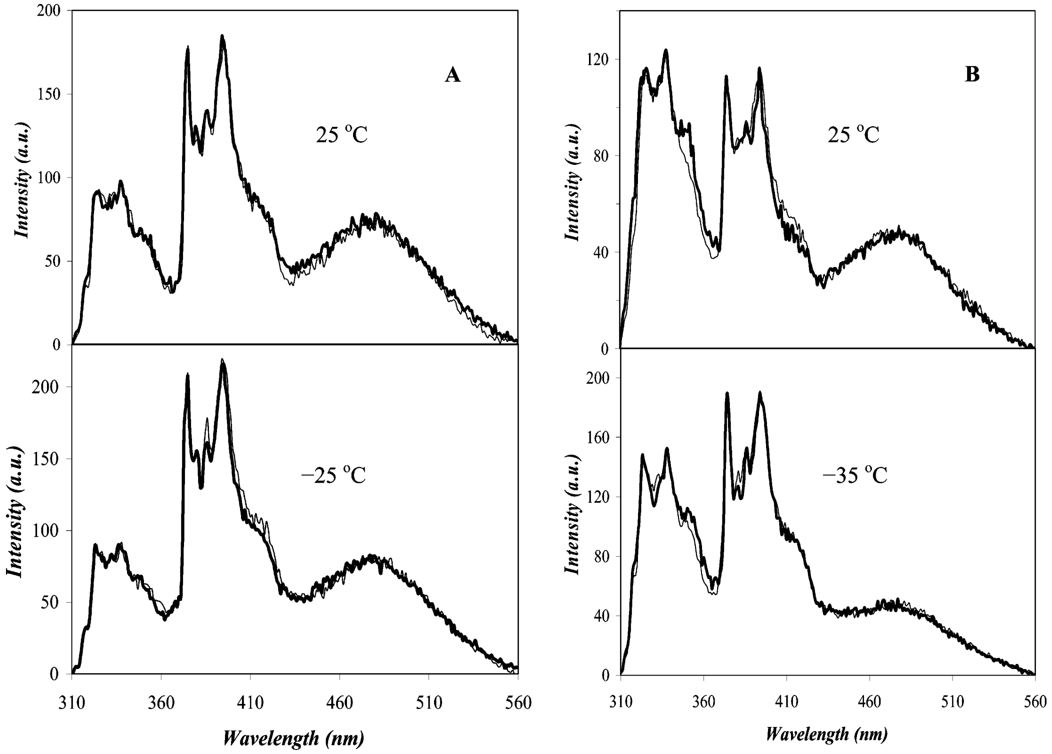

Figure 6. Spectra of EPs obtained from the mixing experiment (thin trace) and from the addition of the two individual spectra (thick trace) in toluene (A, EP-CR; B, EP-NCR). $\lambda_{ex} = 300$ nm.

when the I_{Py}/I_{Np} ratios were normalized to their value at 25 °C, the normalized ratios obtained at 2 g/L overlapped those obtained at 0.1 g/L, as shown in Figure 5. This result suggests that DET affects all I_{Py}/I_{Np} ratios in a similar manner and that this complication seems to be avoided by normalizing the ratios to their value at 25 °C as done in Figure 5. This observation also suggests that the I_{Py}/I_{Np} trends shown for EP-CR in Figure 5 with a polymer concentration of 2 g/L are due to the same phenomenon which affects the [η] and light scattering measurements, performed with polymer concentrations of 1−4 g/L for [η] and 2 g/L for light scattering, namely the formation of crystalline microdomains inside the polymer coils. Since the I_{Py}/I_{Np} ratio vs temperature trends are similar whether the experiments are performed at 0.1 or 2 g/L, the FRET behavior shown in Figure 5 with an EP-CR concentration of 0.1 g/L is due to the formation of microcrystals inside isolated polymer coils. In other words, this microcrystallization process occurs intramolecularly at this concentration.

The experiments carried out so far have established that the labeling of the EPs with fluorescent probes does not affect the behavior of the polymers in toluene (Figures 1−3), that the formation of crystalline microdomains inside the polymer coils induces a contraction of the coil volume (Figures 2 and 5), and that this crystallization-induced contraction of the polymer coil occurs intramolecularly at polymer concentrations smaller than 0.1 g/L (Figure 6). Thus, the EP-CR sample provides an ideal case to study how the formation of crystalline microdomains inside a polymer coil affects the intramolecular formation of excimer between pyrenes randomly attached along the backbone. This effect is now investigated in earnest.

Pyrene Excimer Formation: Steady-State Fluorescence. The fluorescence spectra of the pyrene-labeled EP-CR and EP-NCR in toluene were acquired at temperatures ranging from −35 to 60 °C. They are shown in Figure 7 for Py-EP-CR in toluene. As the temperature decreases, the fluorescence intensity of the pyrene monomer increases while that of the excimer decreases. According to the Birks' scheme,[29] pyrene excimers are formed via the diffusional encounters between a ground-state and an excited pyrene monomer. Since the viscosity of a solvent increases with decreasing temperatures, lower temperatures usually lead to decreased diffusional encounters and excimer emission. Furthermore, increased viscosity reduces the deactivation of the excited pyrene monomer via encounters with solvent molecules and the polymer backbone. As a result, the quantum yield of the pyrene monomer increases with decreasing temperatures, and the pyrene monomer emission is further enhanced.

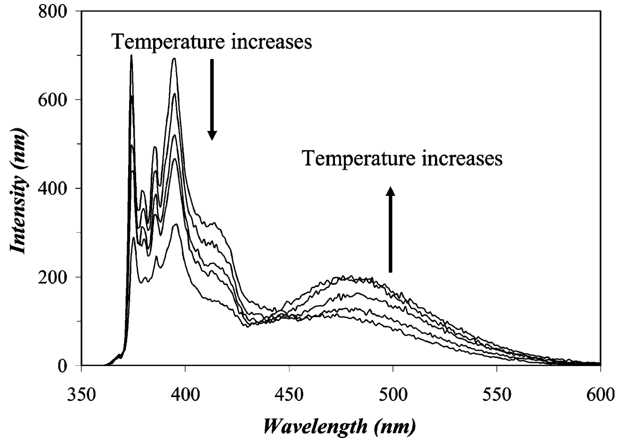

Figure 7. Fluorescence emission spectra of pyrene-labeled EP-CR in toluene as a function of temperature ($\lambda_{ex} = 346$ nm, [pyrene] = 2.5×10^{-6} M, [polymer] = 0.02 g/L).

The steady-state fluorescence spectra of the pyrene-labeled EP samples were acquired at three different polymer concentrations as a function of temperature. As shown in the Supporting Information (cf. Figures SI.3 and SI.4), all polymer solutions were stable during the period where the fluorescence spectra were acquired. The I_E/I_M ratios were calculated, normalized to their value at 25 °C, and plotted in Figure 8. The unnormalized

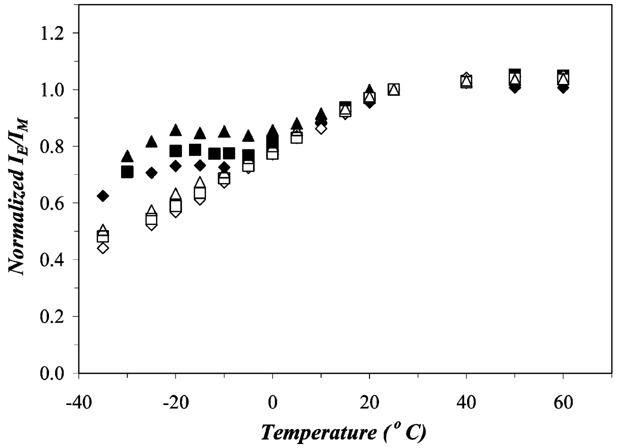

Figure 8. Normalized I_E/I_M ratio of Py-EPs plotted as a function of temperature at various concentrations in toluene (triangles, 0.02 g/L; squares, 0.1 g/L; diamonds, 2 g/L). Full and empty symbols are for Py-EP-CR and Py-EP-NCR, respectively.

I_E/I_M profiles can be found in Figure SI.6 in the SI. In Figure 8, differences in the trends obtained for a given EP sample are small, regardless of polymer concentration. For EP-CR, the I_E/I_M ratio remains constant between 20 and 60 °C. It then decreases with decreasing temperature between −5 and +20 °C. Between −20 and −5 °C, the I_E/I_M ratio remains constant before decreasing further with decreasing temperature for $T < -20$ °C. A very similar trend was observed for EP-NCR between −5 and 60 °C. But instead of plateauing at −5 °C as EP-CR does, the I_E/I_M ratio of EP-NCR decreased continuously with decreasing temperature for temperatures between −35 and +20 °C.

The data shown in Figure SI.6 confirm that the phenomena probed by fluorescence at polymer concentrations of 0.02 and 0.1 g/L are occurring intramolecularly because the I_E/I_M ratio trends obtained at both concentrations overlap very well. An increase in I_E/I_M is usually taken as an indication that intermolecular association is taking place.[30] This result further supports the conclusions drawn from the FRET data shown in Figure 6. At a concentration of 2 g/L, intermolecular excimer formation takes place and the I_E/I_M ratio increases (cf. Figure SI.6). However, the I_E/I_M trends obtained at higher polymer concentration look strikingly similar to those obtained at lower polymer concentrations. This observation is confirmed by normalizing the I_E/I_M ratios to their value at 25 °C as shown in Figure 8. The I_E/I_M traces overlap relatively well except for the plateau region of Py-EP-CR between −20 and −5 °C. The onset of this plateau region appears to be delayed by a few degrees when the polymer concentration increases.

The I_E/I_M vs temperature profiles obtained for Py-EP-NCR in Figure 8 are similar to those observed in other studies of Py-PDMAA in methanol[31] and Py-PS in cyclohexane[32] by Martinho and co-workers and of Py-PDMAA in DMF and acetone by our laboratory.[33] Since the Py-PDMAA and Py-PS samples are noncrystalline, the similar I_E/I_M vs temperature profiles obtained for Py-PDMAA, Py-PS, and Py-EP-NCR reflect the noncrystallinity of EP-NCR, whereas the emergence of a plateau observed only for EP-CR between −20 and −5 °C is certainly a consequence of the formation of microcrystals by EP-CR.

The I_E/I_M ratio obtained with pyrene-labeled polymers usually decreases as the solvent viscosity increases due to a decrease in temperature. This effect is observed for Py-EP-NCR in toluene. The presence of a plateau between −20 and −5 °C for the Py-EP-CR sample in toluene indicates that the decrease in pyrene excimer formation is being hindered. Since the polymer coil of EP-CR shrinks as microcrystals are forming (cf. Figures 2 and 5), the pyrene pendants are brought closer to one another, which promotes pyrene excimer formation. Consequently, pyrene excimer formation increases and the I_E/I_M ratio is larger than it would be, were the formation of microcrystals not taking place. It appears that in the −20 to −5 °C temperature range the increase in I_E/I_M induced by the contracted EP-CR coil offsets the decrease in I_E/I_M caused by the enhanced viscosity so that the I_E/I_M ratio remains constant over this temperature range. When the microcrystallization is completed at −20 °C, the I_E/I_M ratio resumes its decrease with decreasing temperature. The onset temperature (∼−5 °C) where the I_E/I_M ratio of EP-CR plateaus in Figure 8 corresponds to the temperature (∼0 °C) where the exothermic peak of the 50 g/L toluene solution of EP-CR begins to appear in the DSC trace (Figure 1), the intrinsic viscosity begins to decrease (Figure 2), the light scattering intensity begins to increase (Figure 3), and the I_{Py}/I_{Np} ratio of the doubly labeled EP-CR starts to increase steadily (Figure 5). The agreement with respect to the onset temperature obtained from the five experiments consolidates the view that the unique behavior of I_E/I_M exhibited by Py-EP-CR is related to the formation of microcrystals.

Furthermore, according to Birks' scheme,[29] a plot of $\ln(I_E/I_M)$ vs $1/T$ shown in Figure SI.7 yields information about the excimer formation kinetics. For a pyrene-labeled polymer, the I_E/I_M ratio is expected to be proportional to $\langle k_1 \rangle/(k_{-1} + 1/\tau_E)$, where $\langle k_1 \rangle$ is the average rate constant of excimer formation, k_{-1} is the dissociation rate constant which is small at low temperature, and τ_E does not change much with temperature.[34] Consequently, the I_E/I_M ratio is normally found to be proportional to $\langle k_1 \rangle$ at low temperature, and it increases with increasing temperature. At high temperature, k_{-1} is not negligible, and the I_E/I_M ratio passes through a maximum and decreases with increasing temperature.[35] EP-NCR exhibits a linear relationship between $\ln(I_E/I_M)$ and $1/T$ for temperatures smaller than 20 °C. The activation energy (E_a) for the pseudo-unimolecular rate constant $\langle k_1 \rangle$ was calculated for both Py-EPs for $T < 20$ °C. The slope of the straight line yielded E_a values of 8.3 ± 0.2 and 8.5 ± 0.3 kJ/mol for $\langle k_1 \rangle$ for Py-EP-NCR and Py-EP-CR, respectively. These activation energies are close to those calculated for the viscosity of toluene where E_η equals 9.0 kJ/mol. The agreement between the activation energy resulting from the formation of the pyrene excimer, E_a, and the solvent viscosity, E_η, indicates that the excimer formation is diffusion-controlled for $T < 20$ °C. When the temperature is increased above ∼25 °C for both Py-EPs, the dissociation of the pyrene excimer becomes nonnegligible. Thus, the relationship between $\ln(I_E/I_M)$ and $1/T$ is not linear anymore. Similar observations have been obtained with Py-PDMAA in methanol,[31] acetone, and DMF[33] and Py-PS in cyclohexane.[32] However, k_{-1} becomes nonnegligible at ∼45 °C for Py-PDMAA and Py-PS. That k_{-1} becomes nonnegligible at 25 °C for Py-EPs indicates that less energy is required to destabilize the pyrene excimer. This could be due to the bulky succinimide linker of the Py-EP sample which might prevent the pyrene moieties to take the ideal conformation to form an excimer, making the excimer less stable.

In order to investigate how individual polymer coils behave at high polymer concentration, solutions were prepared that contained 0.02 g/L of pyrene-labeled EP copolymers and 2 g/L of unlabeled EP copolymer. Although the overall polymer concentration is relatively large in these solutions, the pyrene-labeled chains are sufficiently dilute to ensure that the fluores-

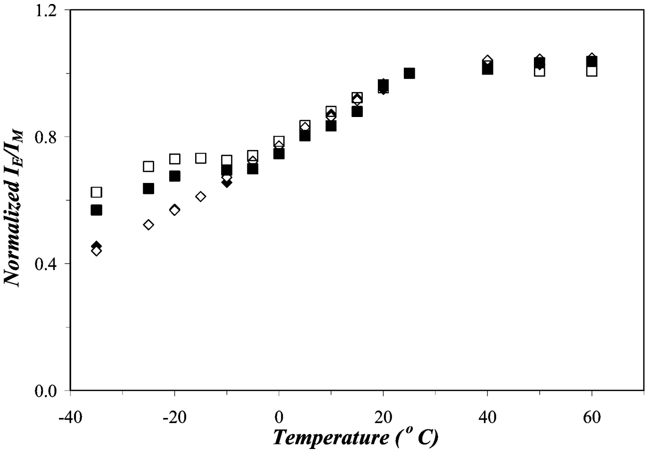

Figure 9. Normalized I_E/I_M ratio of Py-EPs plotted as a function of temperature in toluene (squares, EP-CR; diamonds, EP-NCR). All solutions contained 0.02 g/L of labeled EPs. Full and empty symbols are for solutions with and without 2 g/L of naked EP, respectively.

cence signal of isolated Py-EP coils is being monitored. The results shown in Figure 9 demonstrate that the I_E/I_M ratio vs temperature profiles exhibit the same features whether the unlabeled polymer is added to the solutions or not. This result suggests that the presence of large amounts of unlabeled polymer does not affect the formation of pyrene excimer inside isolated pyrene-labeled chains.

Conclusions

Two EP copolymers were maleated and labeled with fluorescent chromophores such as 1-pyrenemethylamine and/or 1-naphthalenemethylamine. DSC measurements were performed in the solid state and in toluene. It was confirmed that one EP sample is semicrystalline (EP-CR) while the other is noncrystalline (EP-NCR) in both the naked and the labeled forms.

Intrinsic viscosity, light scattering, and fluorescence experiments were carried out in toluene as a function of temperature. It was shown that for either EP in the naked, grafted, or labeled form the intrinsic viscosity of EP-NCR did not change much with temperature between −10 and +45 °C. For EP-CR, the intrinsic viscosity remained constant between 10 and 45 °C while it decreased continuously with decreasing temperature when the temperature was below 10 °C, indicating that the polymer coil of EP-CR shrinks progressively with decreasing temperature.

In the light scattering measurements, very similar scattering intensity vs polymer concentration profiles were observed for EP-NCR and toluene whereas a different profile was obtained for EP-CR, in both the naked and labeled forms. The gradual increase in scattering intensity observed for EP-CR can be accounted for by the formation of microcrystals at temperatures below 0 °C within the ethylene-rich stretches.

Fluorescence resonance energy transfer (FRET) experiments were performed with the doubly labeled EPs in toluene at various temperatures. The I_{Py}/I_{Np} ratio was calculated and normalized to its value at 25 °C for both EPs. The plot of the normalized I_{Py}/I_{Np} ratio vs temperature showed that EP-CR exhibits a more drastic increase in I_{Py}/I_{Np} with decreasing temperature than EP-NCR, regardless of polymer concentration. These trends demonstrated that the polymer coil of EP-CR shrinks more significantly than that of EP-NCR over the temperature range of interest. In addition, FRET measurements established that energy transfer occurs intramolecularly throughout the temperature range of investigation for both doubly labeled EPs at polymer concentrations smaller than 0.1 g/L.

Steady-state fluorescence spectra were acquired for the pyrene-labeled EPs in toluene as a function of temperature. In the plot of I_E/I_M vs temperature, a unique plateau was observed for Py-EP-CR between −20 and −5 °C while no such plateau was observed for Py-EP-NCR. These results imply that the pyrene pendants are more concentrated inside the Py-EP-CR coil between −20 and −5 °C. In other words, the coil of Py-EP-CR is more compact than that of Py-EP-NCR, as expected from the formation of microcrystals. The good agreement among the several transition temperatures observed in the vicinity of 0 ± 5 °C by means of very different experimental techniques such as intrinsic viscosity, light scattering, FRET, and pyrene excimer formation measurements leads one to conclude that microcrystallization occurs around 0 °C for EP-CR in toluene. The fluorescence experiments based on FRET and pyrene excimer formation demonstrate that for polymer concentrations smaller than 0.1 g/L microcrystallization occurs intramolecularly for EP-CR in toluene.

Acknowledgment. This work was supported financially by NSERC, Imperial Oil, and DSM. J.D. is indebted to the CFI funding associated with his Tier-2 CRC award. M.Z. and J.D. thank Prof. J. Soares at UW for using his GPC. M.Z. and J.D. are also indebted to Drs. Martin van Duin and Patric Meessen at DSM in Geleen, The Netherlands, for fruitful discussions. M.Z. and J.D. acknowledge the help of April Wong, who conducted most of the intrinsic viscosity measurements. J.D. thanks Dr. Abdeljalil Assoud and Prof. Holger Kleinke for carrying out the X-ray diffraction measurements.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Booser, E. R. In *Encyclopedia of Chemical Technology*; Mark, H. F., Othmer, D. F., Overberger, C. G., Seaborg, G. T., Grayson, M., Eckroth, D., Eds.; Wiley-Interscience: New York, 1982; Vol. 14.
(2) Rubin, I. D.; Sen, A. *J. Appl. Polym. Sci.* **1990**, *40*, 523−530.
(3) Sen, A.; Rubin, I. D. *Macromolecules* **1990**, *23*, 2519−2524.
(4) Kucks, M. J.; Ou-Yang, H. D.; Rubin, I. D. *Macromolecules* **1993**, *26*, 3846−3850.
(5) Arlie, J. P.; Denis, J.; Parc, G. *Inst. Petr. Paper* 75-006, 1975 (London). (b) Neudoerfl, P. In *Technische Akademie Esslingen*; Bartz, W. J., Ed.; UHREN: Ostfieldern, 1986; pp 8.2-1 to 8.2-15.
(6) Marsden, K. *Lubr. Sci.* **1988**, *1*, 265−280. (b) Ver Strate, G.; Struglinski, M. *J. Polym. Mater. Sci. Eng.* **1989**, *61*, 252−258.
(7) Eckert, R. J. A.; Covey, D. F. *Lubr. Sci.* **1988**, *1*, 65−80.
(8) Delmas, G.; Daviet, V.; Filiatrault, D. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1629.
(9) Filiatrault, D.; Phuong-Nguyen, H.; Delmas, G. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 763.
(10) Filiatrault, D.; Delmas, G. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 773.
(11) Filiatrault, D.; Delmas, G. *Macromolecules* **1979**, *12*, 65−69.
(12) Morimoto, M.; Okamoto, Y. *J. Appl. Polym. Sci.* **1972**, *16*, 2795.
(13) Maderek, E.; Wolf, B. A. *Angew. Makromol. Chem.* **1988**, *161*, 157−173.
(14) Mays, J. W.; Fetters, L. J. *Macromolecules* **1989**, *22*, 921−926.
(15) Elias, H.-G. *An Introduction to Polymer Science*; VCH: New York, 1997.
(16) Stocker, W.; Schumacher, M.; Graff, S.; Lang, J.; Wittmann, J. C.; Lovinger, A. J.; Lotz, B. *Macromolecules* **1994**, *27*, 6948−6955.
(17) Sabino, M. A.; Albuerne, J.; Muller, A. J.; Brisson, J.; Prud'homme, R. E. *Biomacromolecules* **2004**, *5*, 358−370.
(18) Lotz, B. *Adv. Polym. Sci.* **2005**, *180*, 17−44.
(19) Heinen, W.; Rosemoller, C. H.; Wenzel, C. B.; de Groot, H. J. M.; Lugtenburg, J.; van Duin, M. *Macromolecules* **1996**, *29*, 1151−1157.
(20) Zhang, M.; Duhamel, J.; van Duin, M.; Meessen, P. *Macromolecules* **2004**, *37*, 1877−1890.
(21) Mathew, A. K.; Duhamel, J.; Gao, J. *Macromolecules* **2001**, *34*, 1454−1469.
(22) Zhang, M.; Duhamel, J. *Macromolecules* **2005**, *38*, 4438−4446.

(23) Randall, J. C. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29*, 201−317.
(24) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999.
(25) Strate, G. V. *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1986.
(26) Girolamo, M.; Keller, A.; Miyasaka, K.; Overgergh, N. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 39−61.
(27) Simha, R.; Utracki, L. A. *Rheol. Acta* **1973**, *12*, 455−464.
(28) Yekta, A.; Duhamel, J.; Adiwidjaja, H.; Brochard, P.; Winnik, M. A. *Langmuir* **1992**, *9*, 881−883.
(29) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970.
(30) Kim, S. D.; Torkelson, J. M. *Macromolecules* **2002**, *35*, 5943−5952.
(31) Picarra, S.; Relogio, P.; Afonso, C. A. M.; Martinho, J. M. G.; Farinha, J. P. S. *Macromolecules* **2003**, *36*, 8119−8129.
(32) Picarra, S.; Duhamel. J.; Fedorov, A.; Martinho, J. M. G. *J. Phys. Chem. B* **2004**, *108*, 12009−12015.
(33) Zhang, M. Characterization of Ethylene-Propylene Copolymers by Fluorescence. Ph.D. Thesis, Waterloo, 2005, pp 170−213.
(34) Winnik, M. A. *Acc. Chem. Res.* **1985**, *18*, 73−79.
(35) Stevens, B.; Ban, M. I. *Trans. Faraday Soc.* **1964**, *60*, 1515−1523.

MA061730F