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Tze Chi Jao^a; Munmaya K. Mishra^a; Isaac D. Rubin^a

^a Texaco R&D Department, Beacon, NY, USA

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STUDIES ON ETHYLENE-PROPYLENE COPOLYMER IN HYDROCARBON SOLVENTS BY FLUORESCENCE PROBE METHOD

Tze Chi Jao, Munmaya K. Mishra, and Isaac D. Rubin
Texaco R&D Department
P. O. Box 509
Beacon, NY 12508, USA

ABSTRACT

A pyrene fluorescence probe was grafted onto EP copolymer backbone by reacting 1-pyrenebutyrylhydrazine with pendant succinic anhydride groups. Behavior of the pyrene-labelled EP in methylcyclohexane and tetrahydro-naphthalene (tetralin) was studied as a function of copolymer concentration. Ratios of pyrene excimer intensity to its monomer intensity were determined for copolymer solutions with concentrations ranging from 0.02% to 0.6%. The lower ratios in methylcyclohexane than tetralin agreed with viscosities indicating that methylcyclohexane is a better solvent. The plots of the ratio vs. copolymer concentration in both solvents were nonlinear. From these plots, C^* can be estimated. The fine structure of pyrene monomer fluorescence spectra revealed that the copolymer is loosely coiled in both solvents.

INTRODUCTION

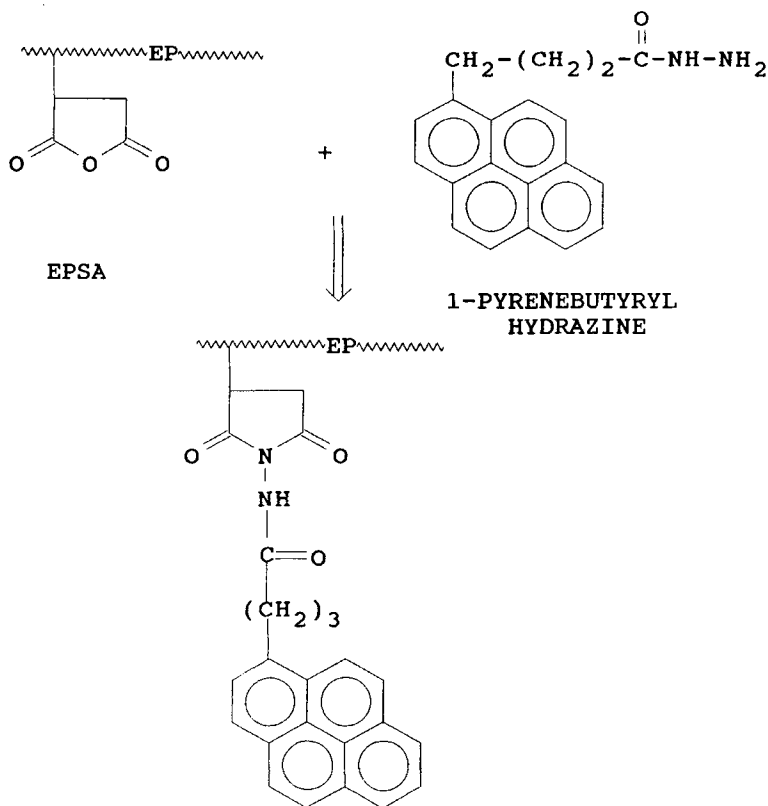
Ethylene-propylene copolymers (EPs) and their derivatives are widely used as viscosity index improvers to extend the temperature range over which mineral oils become satisfactory lubricants for automotive engines.

Earlier work in our laboratory to obtain a better understanding of the solution behavior of these copolymers was focused on the effect of composition and crystallinity of EPs on their low temperature viscosities in model hydrocarbon solvents (1); this was subsequently expanded to include behavior in both naphthenic and paraffinic mineral oils (2,3).

As part of our ongoing effort to understand the behavior of EPs at the molecular level, we have recently initiated a fluorescence probe program to study EP copolymer solutions. Use of pyrene as the probe has been shown to be a powerful tool to study polymer conformation and dynamics in solutions (4,5). By measuring the ratio of pyrene excimer to monomer fluorescence emission intensities, the degree of polymer coiling in solution can be determined. Knowing the degree of polymer coiling, the extent of polymer-solvent interaction can be estimated. The technique has also been employed by Winnik and his coworkers to determine the solubility parameters of polymers. In our study, we have investigated the concentration dependence of solution behavior of an EP copolymer in two different hydrocarbon solvents. This paper reports the preliminary results of this study.

EXPERIMENTAL

The EP copolymer ($\bar{M}_w = 148,000$ and $\bar{M}_w/\bar{M}_n = 3.0$) was prepared by a soluble Ziegler-Natta catalyst composed of ethylaluminum sesquichloride and vanadium oxytrichloride. The methods and procedures for characterizing the copolymer have already been described (1). Maleic anhydride was next grafted onto the EP backbone yielding a product (EPSA) with about 0.8% (w/w) succinic anhydride randomly distributed along the chain. The reaction was carried out in a pressure reactor for 3 hours under an inert environment (200 lbs. of nitrogen pressure) at 155°C in hexane or mineral lubricating oil solution containing about 30 wt% of the EP copolymer. Dicumyl peroxide (1 wt% based on polymer) was used as the initiator. The maleic anhydride amount charged to the reactor was about 3% based on polymer. The polymer was purified by repeated precipitations from heptane by methanol or acetone and freed from unreacted maleic anhydride, and the level of grafting was obtained from FTIR by analyzing and comparing the bands at 1785 cm^{-1} and 720 cm^{-1} . The fluorescence probe was incorporated by reacting the pendant succinic anhydride groups with 1-pyrenebutyrylhydrazine (Molecular Probe, Inc.) using the general scheme shown below.



The reaction was carried out in a resin kettle fitted with a mechanical stirrer, thermometer, and nitrogen inlet and outlet ports. Required amount of EP copolymer with 0.8 wt% (w/w) succinic anhydride groups was dissolved in solvent neutral oil at 160 °C with mechanical stirring under a nitrogen atmosphere to yield about a 15% polymer solution. After the polymer had dissolved, mixing was continued for an additional hour at 160 °C. A slight molar excess of 1-pyrene butyrylhydrazine based on the molar amount of pendant succinic anhydride was added and a reaction effected over 3 hours at 160 °C. The pyrene functionalized polymer was isolated by precipitating the oil solution into methanol. The polymer was then dissolved in heptane. The pyrene-labelled EP (PEP) was purified by repeated precipitations from heptane by methanol or acetone and dried in vacuum at 50 °C for 16 hours (overnight). It

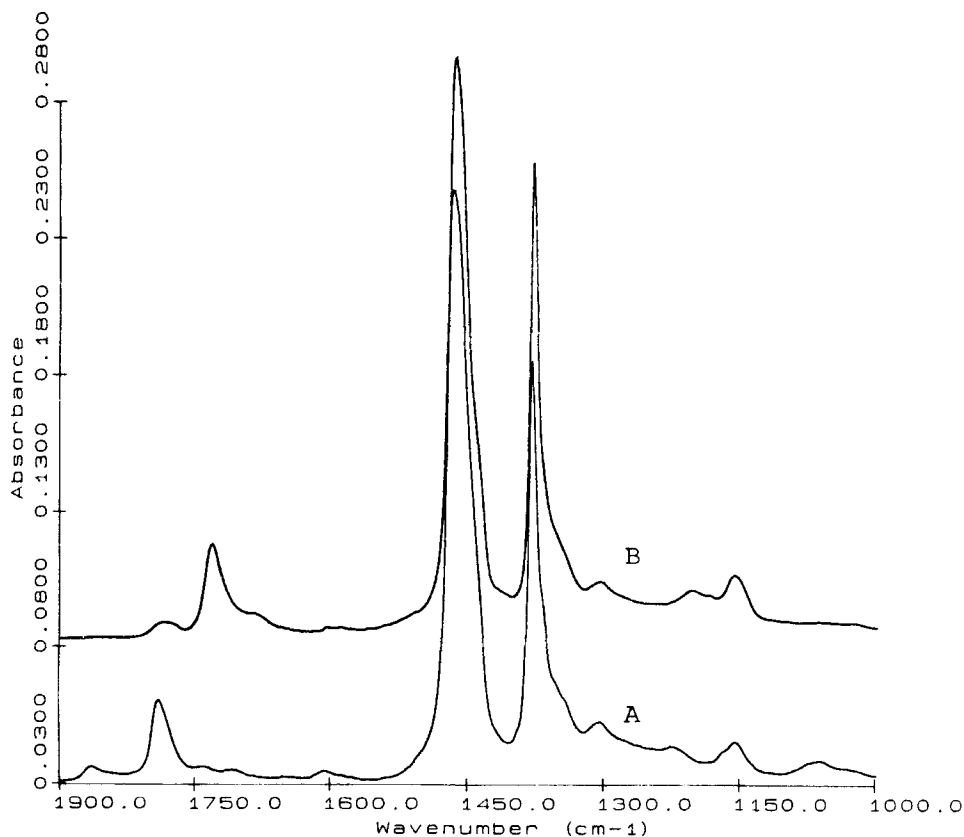


Figure 1. FTIR of EPSA (A) and EPSA reacted with 1-pyrenebutyryl hydrazine (B).

was analyzed on a Nicolet 510 FT-IR spectrophotometer. The absorbance at 1785 cm⁻¹ for the carbonyl group of the succinic anhydride had disappeared and a new absorbance at 1730 cm⁻¹ for the carbonyl group of the imide appeared (Figure 1), showing quantitative conversion of the succinic anhydride to imide.

The two solvents in which the measurements were carried out, 99+% anhydrous methylcyclohexane and 99% 1,2,3,4-tetrahydronaphthalene (tetralin), were used as received (Aldrich Chemical). Copolymer concentrations ranged from 0.02 to 1.0 gm/100 ml; corresponding pyrene concentrations were 1.6×10^{-5} to 8.0×10^{-4} M.

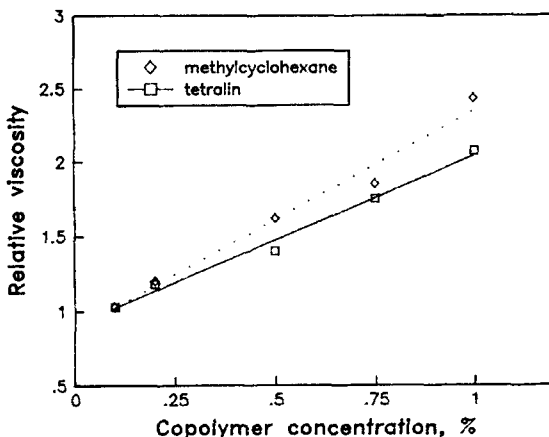


Figure 2. Relative viscosity of PEP at 30°C in two hydrocarbon solvents.

Viscosity measurements were obtained at 30°C on a Haake Rotavisco Rotational Viscometer using the sensor system ME 30. For fluorescence measurements, the solutions were deoxygenated by repeated freeze-thaw cycles on a high vacuum system at 10(-6) torr. Steady-state fluorescence measurements were carried out on a Perkin-Elmer MPF 66 Fluorospectrophotometer at 20°C; the excitation wavelength for the emission system was 340 nm. Emission spectra were recorded perpendicularly to the excitation beam. The spectral slits were set between 1 and 2 nm. No spectral filters were used and each spectrum represents an average of 3 scans. UV absorption measurements were carried out with a Hewlett-Packard 8450A UV-Vis spectrophotometer at 340 nm.

RESULTS AND DISCUSSION

Figure 2 shows the relative viscosities of PEP in both solvents at concentrations of 0.1 to 1.0 gm/100 ml and shear rate of 100 sec(-1). As can be seen, the copolymer is more extended in methylcyclohexane than in tetralin. This is similar to the results for the EP backbone used in synthesis of the pyrene derivative (1) and indicates that the side groups have no significant effect on solubility.

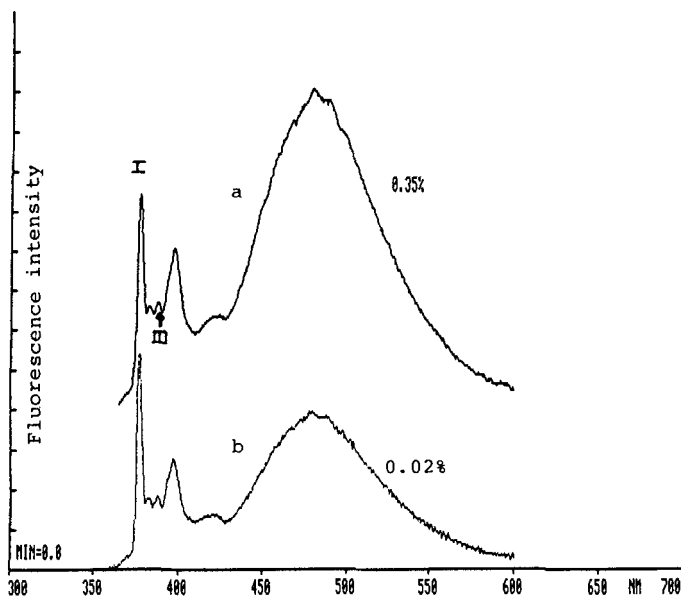


Figure 3. Fluorescence spectra of PEP in methylcyclohexane.

The fluorescence emission spectra of PEP solutions in methylcyclohexane at pyrene concentrations of 2.8×10^{-4} and 1.6×10^{-5} M, equivalent to copolymer concentrations of 0.35 and 0.02% (w/v), respectively, are shown in Figures 3a and 3b. Figures 4a and 4b give the corresponding spectra in tetralin. In all cases, each fluorescence emission spectrum contains a fine structure of monomer emission with a band maximum centered around 377 nm and a structureless excimer emission band centered around 480 nm. Two types of information can be extracted from these spectra: 1) the ratio of excimer to monomer fluorescence intensities, and 2) the ratio of band III to band I of the fluorescence intensities from the fine structure of pyrene monomer emission. The first ratio has been shown to correlate with the "goodness" of solvent (4), while the second ratio was found to be sensitive to the polarity of the solvent medium (6).

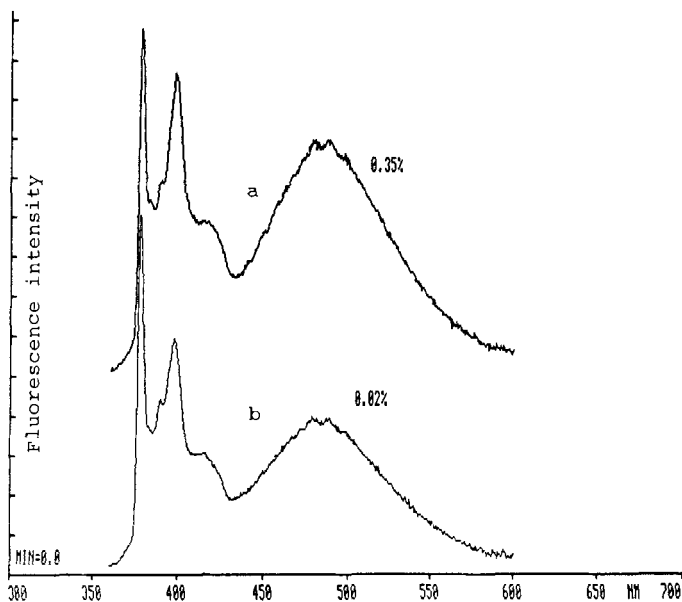


Figure 4. Fluorescence spectra of PEP in tetralin.

The plots of the ratios of η_0 (I_e/I_m) obtained from PEP as a function of polymer concentration in methylcyclohexane and tetralin are shown in Figure 5, where η_0 , I_e and I_m are the solvent viscosity, pyrene excimer emission intensity and monomer emission intensity, respectively. The lower ratios in methylcyclohexane than in tetralin for all polymer concentrations indicate that methylcyclohexane is a better solvent than tetralin. This conclusion agrees with the viscosity measurements shown in Figure 2.

More interesting features in Figure 5 are that each plot can be fitted with two straight lines. In both cases, below 0.2% copolymer concentration the ratio is essentially constant over a ten-fold increase in concentration, while above 0.2% the ratio increases linearly. The behavior at low concentrations can be attributed to intramolecular interaction as the dominant process (5), while at high polymer concentrations

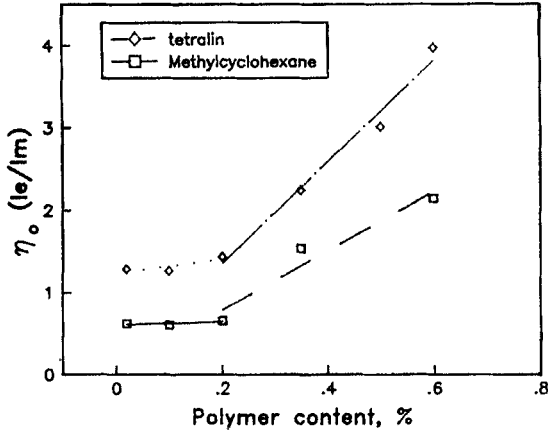


Figure 5. Plots of $\eta_0 (I_e/I_m)$ vs polymer content in methylcyclohexane and tetralin.

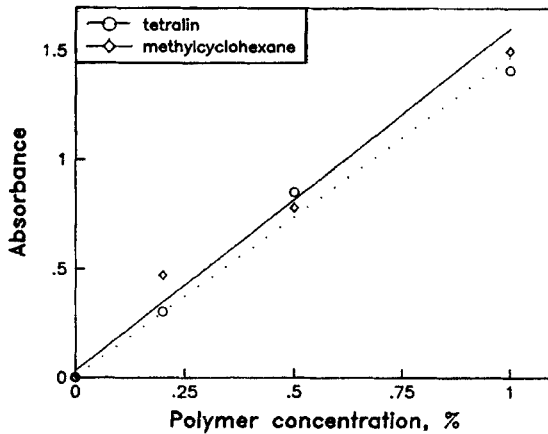


Figure 6. Plots of UV absorbance vs polymer concentration in methylcyclohexane and tetralin.

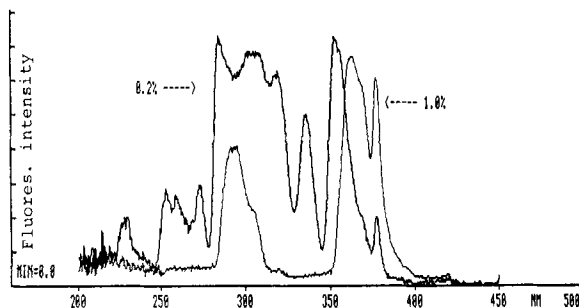


Figure 7. Excitation spectra of PEP in methylcyclohexane in two concentrations.

the total excimer intensity is the contribution of both intra- and intermolecular interactions. Thus, the intersection of the two lines in Figure 5 seems to represent C^* , the crossover point between dilute and semidilute regimes, below which the chains are essentially isolated and above which they interpenetrate each other.

Comparing the ratios of band III to band I of the monomer emission in the two solvents, we can see that the ratios in tetralin are significantly lower than in methylcyclohexane (e.g., at 0.02% the ratios are 0.58 and 0.85 in tetralin and methylcyclohexane, respectively) indicating that the probe is seeing a more polar environment. This means that the polymer even in the tetralin solution is loosely coiled. If the polymer coils were tightly packed with the probe completely shielded by the polymer backbone, the ratio would be close to that observed in the methylcyclohexane.

When investigating polymer solution behavior at high concentrations it is necessary to check carefully the linear dependence of UV absorption and self absorption of fluorescence emission. No UV absorption frequency shift was observed in methylcyclohexane; similar results were obtained in tetralin. The plot of UV absorbance vs. concentration, as shown in Figure 6, follows Beer's law in the concentration range studied. We found that there are no UV spectral structural changes or any absorption frequency shifts for different concentrations of PEP in methylcyclohexane or tetralin. Figure 7 shows that the excitation spectra of PEP de-

pend on the polymer concentration. In general, the spectral structural changes are accompanied by the spectral band shift towards longer wavelength. Such spectral changes are believed to be caused by excess absorption of the excitation light at 340 nm by the solutions as the concentration increases (7). Since fluorescence emission is generally more sensitive than absorption, the changes in the excitation spectra of pyrene could also be induced by the ground state complex formation despite the fact that we did not observe that from the UV absorption spectra. The absorption and emission spectra of pyrene in an inert solvent like cyclohexane were found not to overlap significantly (8). Thus, even though the excitation spectra are distorted, such distortions are not expected to affect the structure of emission spectra because the absorption and emission spectra do not overlap significantly (7).

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