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I. D. Rubin[a]; A. J. Stipanovic[a]; A. Sen[ab]
[a] Texaco Research Center, Beacon, NY [b] Dow Chemical Co., Midland, MI

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MACROMOLECULAR REPORTS, A28(SUPPL. 1), 75-83 (1991)

STRUCTURE-PERFORMANCE CHARACTERISTICS OF ETHYLENE-PROPYLENE COPOLYMERS IN OIL

I. D. Rubin, A. J. Stipanovic and A. Sen*
Texaco Research Center, Box 509, Beacon, NY 12508
***Dow Chemical Co., Midland, MI 48674**

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ABSTRACT

A study was made of the viscosities of three ethylene-propylene copolymers in a naphthenic base oil. Two of the copolymers contained, respectively, 60 and 70 mol% ethylene and were amorphous while the third had 80 mol% ethylene and was partially crystalline. At room temperature, the solutions of both amorphous and partially crystalline copolymers were Newtonian. At low temperatures, the solution of the partially crystalline copolymer became non-Newtonian and gave viscosity values which were much lower than expected on the basis of molecular weight. These results are interpreted in terms of formation of ordered domains or aggregates in the solutions of the partially crystalline copolymers at low temperatures.

INTRODUCTION

Ethylene-propylene (EP) copolymers are widely used in formulating multigrade crankcase oils. Polymer solutions generally show non-Newtonian behavior and decreasing viscosity with increasing shear rate (1). This behavior is due to orientation of the large polymer molecules in the direction of flow. Consequently, to understand the behavior of EP oil solutions, it becomes important to measure their viscosities under conditions of temperature and shear similar to those encountered in use. This paper describes such a study on EP copolymers differing in molecular weight, ratio of ethylene to propylene and

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crystallinity to determine how these variables affect their viscosities in oil.

EXPERIMENTAL SECTION

The EPs were prepared by conventional Ziegler-Natta polymerization using soluble catalysts. The three copolymers investigated in this study were used in some of our previous work and determinations of molecular weights, polydispersities, melting points (Tm) and crystallinities have already been described (2). C-13 NMR characterization for ethylene contents, mean number of ethylene units in sequences of 3 or more, $\bar{N}$, and the fraction of ethylene sequences containing 3 or more ethylenes, En ≥3, are likewise given in the above reference.

Viscosity measurements at low shear rates (0-300 1/s) were carried out with a Haake Rotovisco Rotational Viscometer (RV-100, CV-100, LV-100) at 25, -15 and -20° C. Kinematic viscosities, Cold-Cranking Simulator (CCS) and Mini-Rotary Viscometer (MRV) tests were run using the procedures of ASTM D 445, SAE J 300 and D 4684, respectively. All viscosities were measured in N-100 Pale Oil, a typical naphthenic oil at 1% (w/v).

RESULTS

Molecular Characterization of EP Copolymers

The significant characteristics of the copolymers used in this study are listed below in Table 1.

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Table 1. Molecular Characteristics.

	$\bar{M}_w \times 10^{-3}$	Pd = $\frac{\bar{M}_w}{\bar{M}_n}$	Ethylene Mole (%)	$\bar{N}$	En ≥3	Tm (°C)	Crystallinity(%)	
	GPC		NMR			DSC	DSC	x-Ray
VI-1	148.1	2.9	60	4.2	0.35	-	none	-
VI-2	191.9	3.4	70	4.8	0.56	-	none	-
VI-3	207.3	3.6	80	6.5	0.62	45	9.3	8.4

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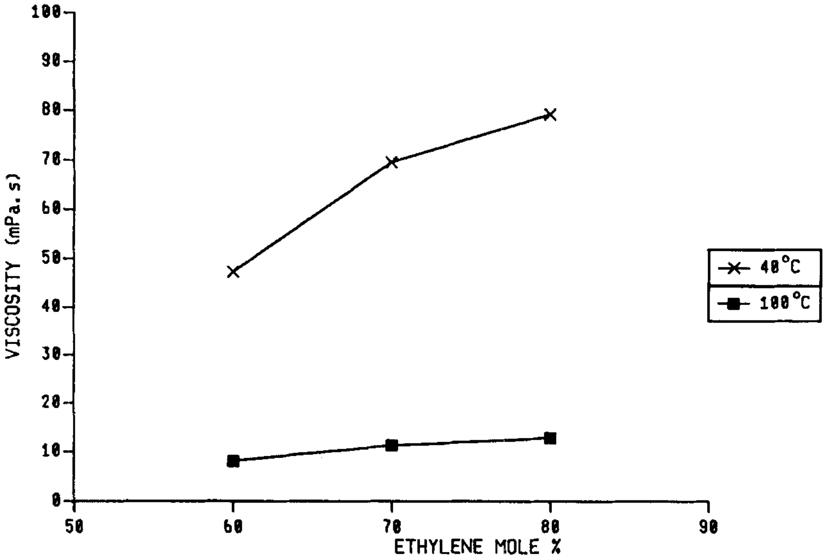

Fig. 1. Kinematic viscosities of the EPs.

As shown, weight average molecular weights range from about 148,100 to 207,300 and molecular weight distributions are 2.9 to 3.6. The mean number of ethylene units in sequences of 3 or more and the fraction of these sequences increase with the amount of ethylene. Wide angle x-ray diffraction in conjunction with differential scanning calorimetry (DSC) shows that VI-3 with 80 mol% ethylene contains about 9% of crystalline material. The copolymers with 60-70 mol% ethylene are amorphous.

Solution Rheology

Important factors which affect solution viscosity of copolymers include, in addition to those which are pertinent for homopolymers, chemical composition, homogeneity, and length of sequences of chemically identical monomer units (3,4). Figure 1 shows the kinematic viscosities of the EPs in the oil at 40 and 100° C. As expected, they increase with molecular weight (5).

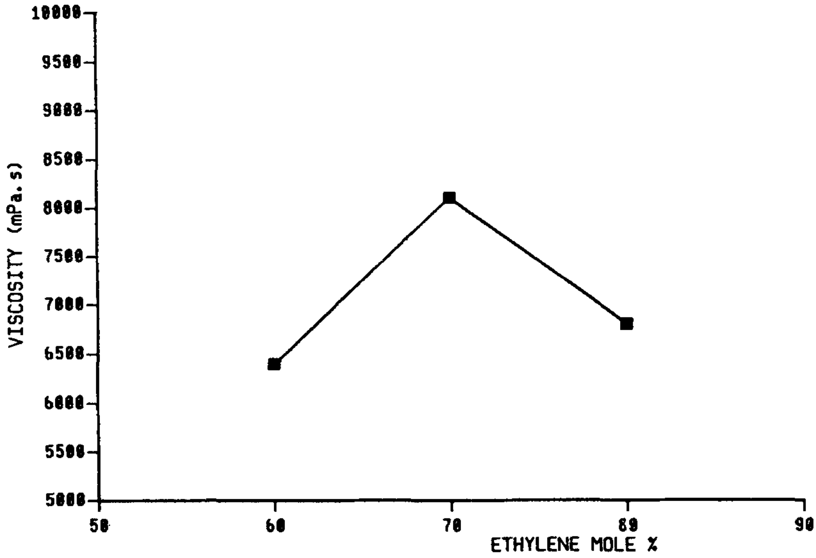

Fig. 2. MRV data on the EPs at -25° C.

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Shear rates encountered by engine oils in the inlet tube section of a car's oil pump are very low, about 15 1/s (6). The ease of pumping oil at low temperatures under such low shear rates is simulated by the mini rotary-viscometer (MRV). The effect of VI improver composition on the MRV viscosities at -25° C is shown in Figure 2. At this temperature, the situation is very different from that in Figure 1. Here, the viscosity of the partially crystalline VI-3 is lower than that of VI-2 with 70% ethylene even though VI-3 has the higher molecular weight. These data reveal that molecular weight is the predominant influence on the solution viscosities of the EPs at high temperatures; however, as temperature is lowered, parameters related to copolymer composition and structure such as ethylene contents, size and number of ethylene sequences, and crystallinity gain in importance.

To obtain better understanding of the effect of shear rate on the solution viscosity of the EPs at low

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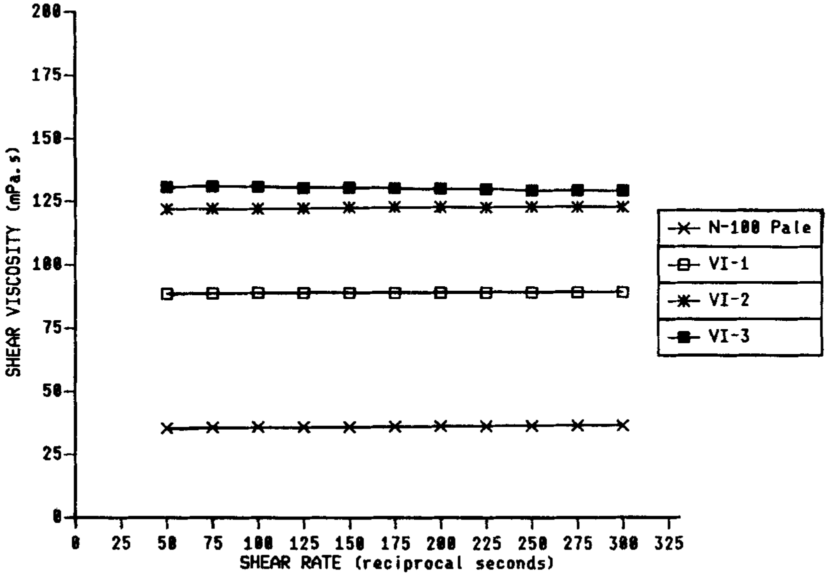

Fig. 3. Shear viscosities of the EPs at 25° C.

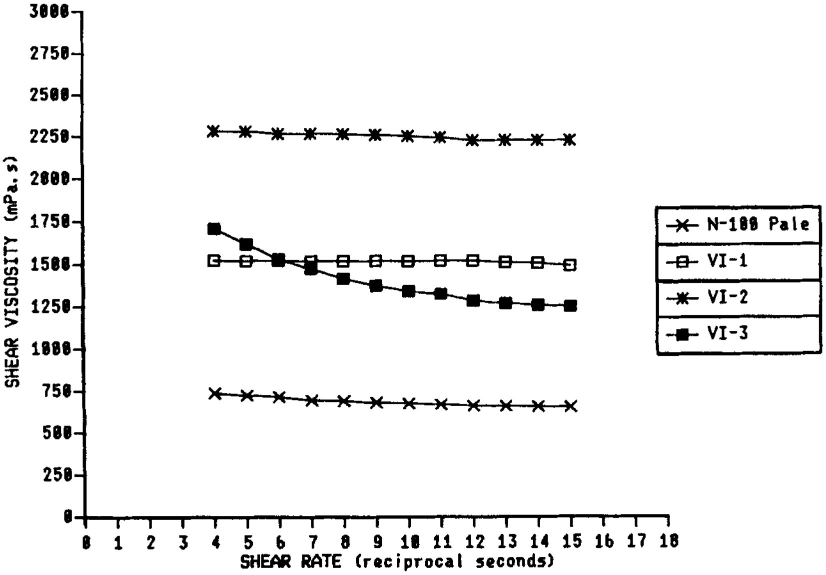

Fig. 4. Shear viscosities of the EPs at -15° C.

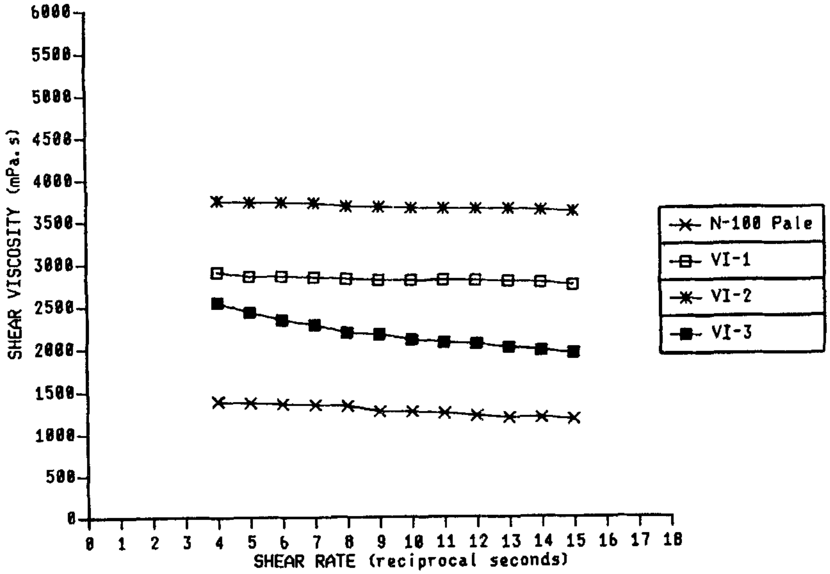

Fig. 5. Shear viscosities of the EPs at -20° C.

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shear, we measured shear stress τ as a function of the shear rate γ. Shear viscosities were calculated using the expression $\eta = \tau/\gamma$. The solution viscosities of the VI improvers under different shear rates at 25, -15 and -20°C are plotted in Figures 3, 4 and 5. As Figure 3 shows, at 50 to 300 1/s and 25° C, the solutions show Newtonian behavior. Even for the highest molecular weight VI-3, viscosity values are independent of shear rate and they increase with molecular weight of the EPs.

Figures 4 and 5 show the shear viscosities at -15 and -20°C at shear rates of up to 15 1/s, where the significant changes occur. For the two amorphous copolymers with 60 and 70 mol% ethylene, viscosities are independent of shear rate but directly related to molecular weights while the solutions of VI-3 are non-Newtonian. The viscosities of VI-3 are lower than those of VI-1 and VI-2 at -20° C at all shear rates and at -15° C between 6 and 15 1/s.

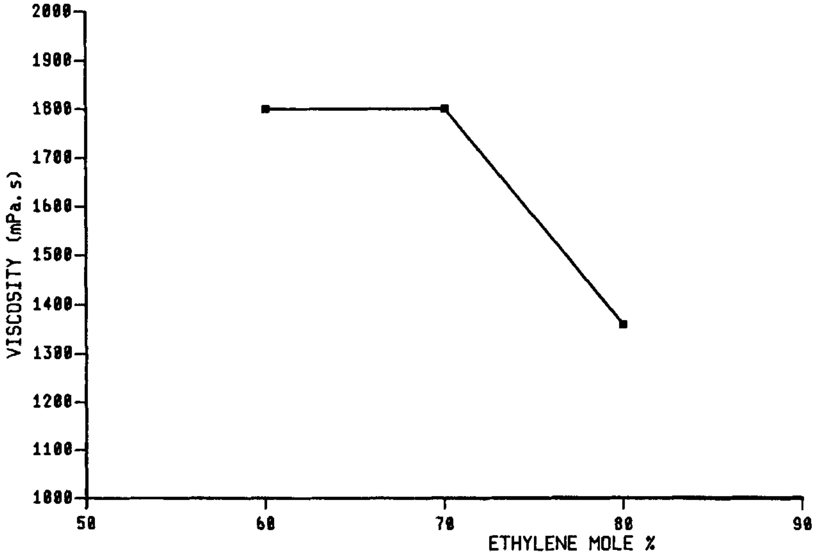

Fig. 6. CCS data on the EPs at -20° C.

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CCS data at -20°C are shown in Figure 6. The CCS was designed to predict performance of oils during cranking when a car is started. The shear rates applied to the samples were between 4000 to 5000 1/s. As shown, the CCS result does not change on increasing the ethylene concentration from 60 to 70 mol% but decreases from 1800 to 1350 mPa.s upon further increase to 80%.

DISCUSSION

The results obtained at low shear rates (the kinematic viscosities at 40 and 100°C and the MRV data at -25°C) indicate that the EPs discussed in this paper can behave in two distinct ways in a naphthenic base oil at low temperature. With the high ethylene content VI-3, polymer-solvent interaction is poor, the dimensions of the copolymer are small and viscosity is low. But for VI-1 and VI-2, polymer-solvent interaction is good, the expansion of the molecule is appreciable, and the viscosity is much higher. Previous work in our laboratory with pure hydrocarbon

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solvents showed that the solubility of the copolymers discussed in this paper was quite sensitive to structural variations of the solvent and composition and structure of the EP (2). A study of the variation in intrinsic viscosities with temperature for ethylene-propylene copolymers by Arlie et al (7) yielded similar results.

It is well accepted that the dependence of non-Newtonian viscosity on shear rate at relatively low shear is associated with the presence of entanglements (1,8,9). The non-Newtonian behavior of the solution of VI-3 at low temperature can be explained by considering these entanglements. The number of entangements and, therefore, their density in solution decrease rapidly with increasing shear rate as the energy required to break most of them is very low. Thus, even at low shear rates one may observe reduction in viscosity due to breakage of entanglements. Changes in copolymer composition and structure may affect the density of entanglements and the energy required to break them, and thus the rheological properties of the solution. The low viscosities shown in Figures 4 and 5 for VI-3 with longer ethylene blocks and some crystallinity indicate that it can orient itself in the direction of flow more effectively than the amorphous copolymers. This means that the EP copolymer with small amount of crystallinity may form shear sensitive microcrystalline domains which are effective in reducing the entanglement density at low temperature and at rather low shear rates below that found in the solutions of the amorphous VI-2 and VI-3. For the amorphous copolymers, the entanglements do not change in the shear rate interval studied and their solutions show Newtonian behavior.

Although it is clear from our data that ethylene sequences sufficiently long to form even very small amounts of crystallinity are responsible for the rapid decrease in solution viscosity at low temperatures, the exact nature of their involvement has yet to be fully elucidated. We believe that at low temperatures the longer ethylene sequences form aggregates or partially ordered domains leading to contraction of the copolymer molecules and decrease in viscosity (11,12). These ordered domains, as discussed above, appear to affect the intermolecular entanglements, making it easier to break them and reduce their number to below that present in similar amorphous copolymers.

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