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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Schulz, D. N. and Bock, J.(1991) 'Synthesis and Fluid Properties of Associating Polymer Systems', *Journal of Macromolecular Science, Part A*, 28: 11, 1235 – 1243

To link to this Article: DOI: 10.1080/00222339108054096

URL: <http://dx.doi.org/10.1080/00222339108054096>

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SYNTHESIS AND FLUID PROPERTIES OF ASSOCIATING POLYMER SYSTEMS

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ABSTRACT

This paper reviews the synthesis and fluid properties of several associating polymer systems. Both hydrocarbon-soluble and water-soluble associating polymers are described. The hydrocarbon-soluble associating polymers are based upon functional polyoctene copolymers. The water-soluble associating polymers are based upon polyacrylamide polymers containing hydrophobic groups.

INTRODUCTION

Normally when one considers advanced materials, one thinks of materials with high performance solid-state properties; e.g., mechanical strength, electrical conductivity, nonlinear optical properties. However, advanced materials can also be fluids, and polymers can be the agents that convert them from simple fluids to high performance ones. A small amount of polymer can have a profound effect on fluid properties; e.g. viscosification, drag reduction, antimisting.

Associating polymers have special benefits in controlling such fluid properties. This paper examines the synthesis and fluid properties of

several associating polymer systems. Both hydrocarbon-soluble and water soluble associating polymers are described.

EXPERIMENTAL

Synthesis

Hydrocarbon-soluble associating polymers, such as poly(1-octene-*co*-methyl undecanoate), poly(1-octene-*co*-undecanoic acid), and interpolymer complexes of poly(1-octene-*co*-undecenoic acid) with poly(styrene-*co*-vinyl pyridine), were prepared according to the methods of our previous report [1]. Water-soluble associating polyacrylamides were synthesized by micellar polymerization or by the use of surfactant macromonomers per our previous reports [2-6].

Solution Properties

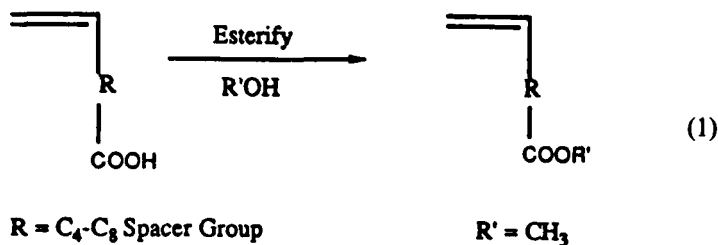
Shear viscosities were measured on a Haake or Contraves viscometer, and elongational viscosities were measured by the tubeless siphon method [1-6].

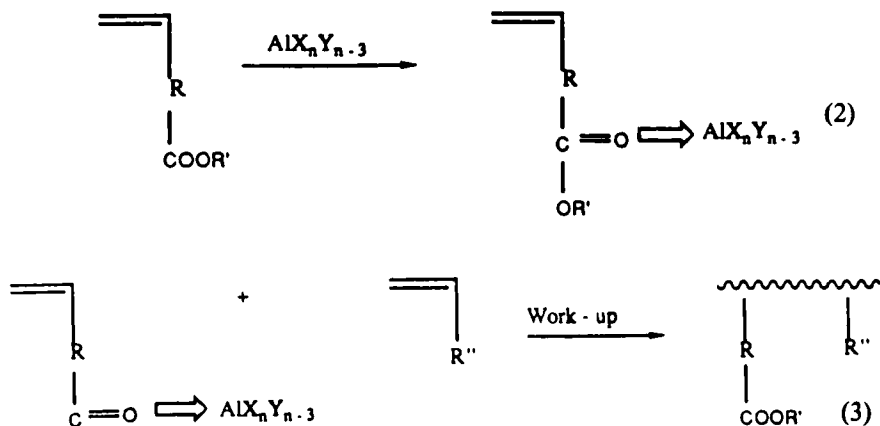
DISCUSSION

Synthesis/Chemistry

The hydrocarbon-soluble associating polymers of this work are based upon functional alpha-olefin polymers. These polymers are prepared by two special Ziegler-Natta polymerization methods that overcome catalyst poisoning.

In the first method, we [7] and others [8-12] have found that Lewis acid precomplexed ester monomers are good carriers for the carboxyl functionality in Ziegler-Natta polymerization (Eqs. 1-3).

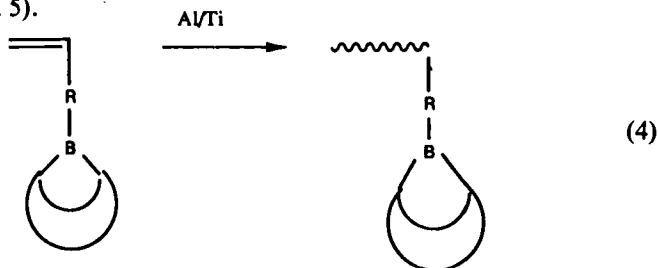


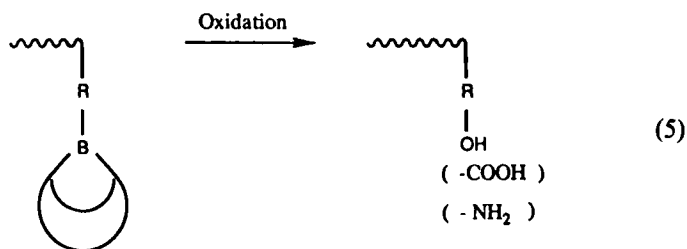


Specifically, carboxyl functional alpha-olefins are reacted with alcohols to form the corresponding esters. The ester monomers have a lower reactivity toward Ziegler-Natta catalysts than do carboxylic acid groups. The ester groups are further protected by precomplexation with aluminum compounds. The order of stability [1] of the ester-aluminum complexes was determined by IR to be TEAL \ll DEAL $<$ EADC $<$ AlCl₃. The complex with TEAL is quite weak; the complex with AlCl₃ is too strong and forms an insoluble complex.

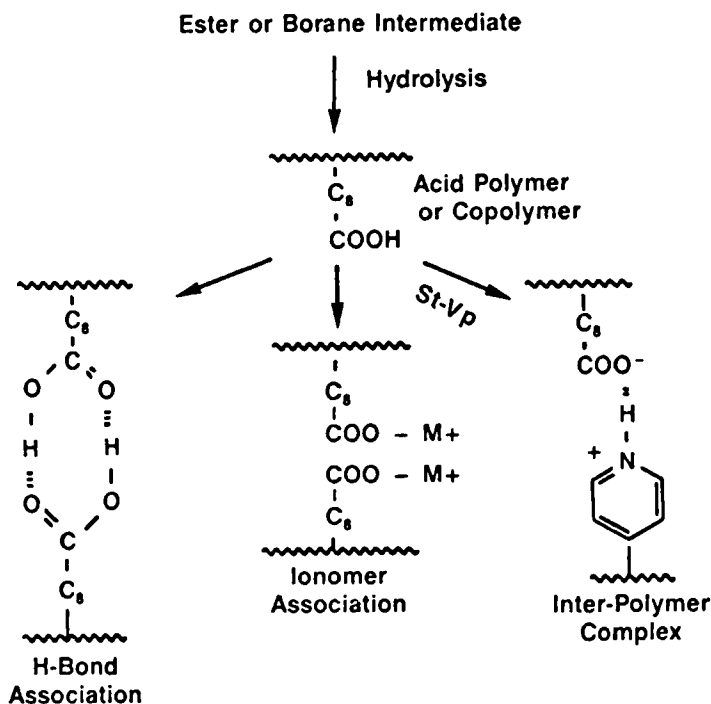
The resulting masked monomers can be homopolymerized or copolymerized with other alpha-olefins. In our case the ester monomer is copolymerized with the long chain alpha-olefin, 1-octene. The presence of the spacer group R is important for two reasons. First, it minimizes the amount of free radical side reactions. Second, the comonomer reactivity ratios are more favorable when R and R' are similar (Eq. 3). Since R'' is a C₆ group, R should preferably lie between 4 and 10 carbon atoms [9-12].

An alternative Ziegler-Natta method for synthesizing functional alpha-olefins is the use of borane-containing monomers and polymers [13] (Eqs. 4 and 5).





Once the ester or borane is prepared, it is easily converted to an acid copolymer by hydrolysis. However, we have found that the ester method is preferred for generating carboxyl functional polymers. The acid groups, in turn, can self-associate via hydrogen bonding, can be neutralized to form ionomers, or can be titrated with basic polymers, e.g., polystyrene-*co*-vinyl pyridine, to form interpolymer complexes (Scheme 1).

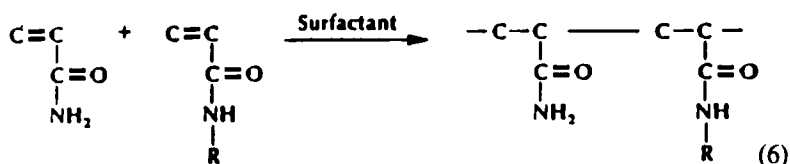


SCHEME 1.

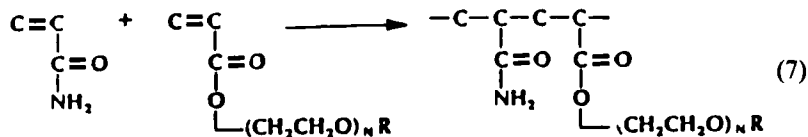
Whereas hydrocarbon polymer backbones can utilize H-bonding, polar, or ionic groups for associations, water-soluble polymers require different mechanisms of interactions because of the high solvation power of water. One such mechanism is hydrophobic association. The hydrophobically associating polymers of this study are based upon polyacrylamide backbones containing long chain alkyl or alkyl/aryl groups.

Hydrophobically associating polymers are difficult to synthesize because of the problem of mixing together oil-soluble and water-soluble monomers. This synthetic hurdle is overcome by the use of micellar copolymerization [2-5] or by the use of surfactant macromonomers [6].

In the micellar copolymerization method, an oil-soluble acrylamide, e.g., C_g-alkyl acrylamide (RAM), is solubilized in the aqueous phase by suitable surfactant(s) (Eq. 6). The main problem with this method is the need for substantial amounts of external surfactant for the solubilization process.



On the other hand, in the surfactant macromonomer method, water-soluble (or dispersible) surfactant and hydrophobe (R) are built into the macromonomer. Consequently, no external surfactants are needed to solubilize the hydrophobic R group. A comparison of typical recipes for synthesizing RAM and PAM-Surf polymers is shown in Table 1 [14].



Fluid Properties

Although the mechanisms of associations of the various polymers of this study are quite different, many of the effects on fluid properties are similar. For example, both the hydrocarbon-soluble associating polymers [e.g., poly(1-octen-*co*-undecanoic acid)] and its interpolymer complexes, as well as the water-soluble associating polymers (e.g., RAM and

TABLE 1. Synthesis of Hydrophobically Associating PAM's Typical Recipes^a

RAM (micellar PZN)	PAM—Surf (surfactant macromonomer)
470.7 g H ₂ O	500 mL H ₂ O
1585 g Sodium dodecyl sulfate	30.0 g Acrylamide
14.76 g Acrylamide	1–5 g Nonyl phenoxy (ethoxy) acrylate
0.288 g Octyl acrylamide	
Above heated to 50°C	Above heated to 50°C
0.01 g K ₂ S ₂ O ₈	0.01 g K ₂ S ₂ O ₈ added

^aD. N. Schulz, in *Water-Soluble Polymers* (ACS Symposium Series 467, S. Shalaby, G. B. Butler, and C. McCormick, eds.), American Chemical Society, Washington, D.C., 1991, pp. 57–73.

PAM-Surf) show enhanced shear viscosity above the overlap concentration, C^* , and lowered viscosity below the overlap concentration compared with the nonassociating polymers (Fig. 1) [1–6]. Also, there is a tendency for both the hydrocarbon- and water-based associating polymers to show shear thickening rheology [1–6] (Fig. 2). Similar effects have been observed for other ionically associating polymer systems [15]. This tendency of associating polymers to show shear thickening rheology has also been treated theoretically [16].

Associating polymers also tend to have enhanced extensional viscosities compared to their nonassociating counterparts. Such extensional viscosities are further increased by shear [1] (Fig. 3). As such, they tend to be candidates for antimisting and drag-reducing agents because such phenomena are related to extensional viscosity [1].

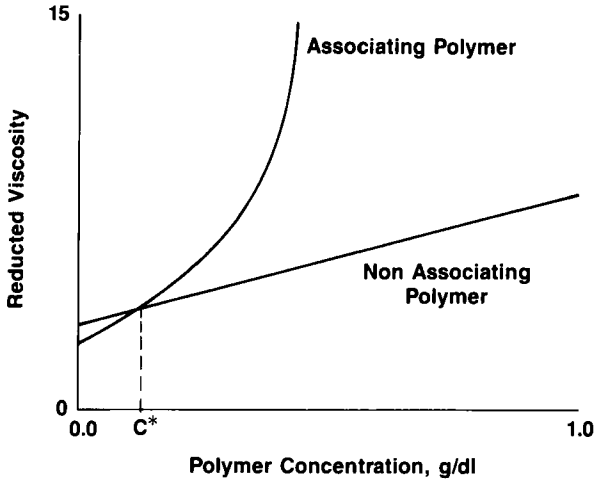


FIG. 1. Reduced viscosity-concentration plot for typical associating polymer vs nonassociating polymer. C^* is the overlap concentration.

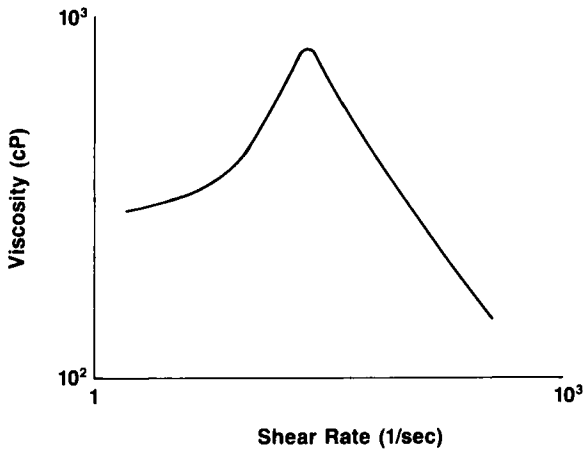


FIG. 2. Viscosity-shear rate plot for a typical associating polymer.

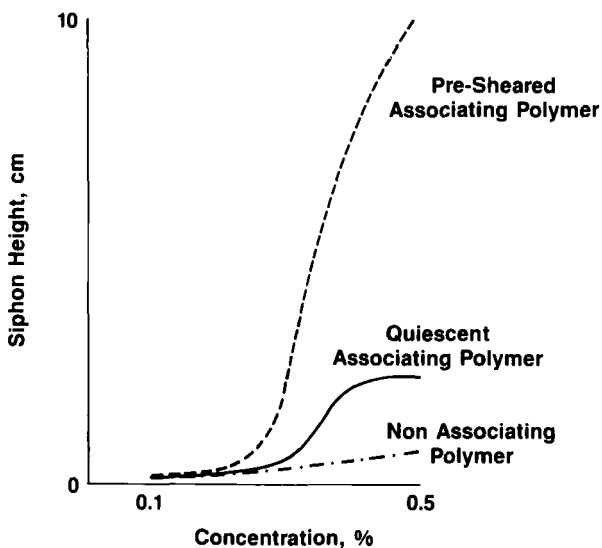


FIG. 3. Extensional viscosity vs concentration plot for quiescent associating polymers, presheared associating polymers, and nonassociating polymer. Extensional viscosities are measured by tubeless siphon height.

ACKNOWLEDGMENTS

Since this paper summarizes the similarities and differences of several different hydrocarbon- and water-soluble associating polymer systems, it embodies the able contributions of a number of people. For example, the synthetic contributions of J. Kaladas, K. Kitano, T. C. Chung, and S. R. Turner, and the fluid characterization work of I. Duvdevani, D. B. Siano, S. Pace, J. Eckert, and R. Kowalik are gratefully acknowledged.

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