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Novel Electro-responsive Property of Polyether-polycarbamate Solution

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A polyether-polycarbamate copolymer was prepared by condensation of polypropylene glycol and 4,4'-diphenylmethane diisocyanate. Shear viscosity and dynamic viscoelasticity measurements under an external electric field elucidated that both the viscosity and storage modulus of the copolymer solution reversibly decrease responding to an electric field. This unique response is opposite to the characteristics of so-called electrorheological fluids.

Electrically induced reversible 'solidification' of a fluid is known as the electrorheological (ER) effect.[1, 2] The fluids exhibiting ER effect, i.e. ER fluids, are expected to be new materials capable of direct transformation of electric signals into mechanical force. Most ER fluids are two-phase systems composed of solid particles and oils. Such suspensions are, however, not stable because of particle sedimentation and/or aggregation. Utilization of homogeneous systems[3, 4] can eliminate the problems due to the particles, but the obtained ER effect was generally smaller than that of suspensions. Recently some liquid crystal polymers (LCP) have been found to show remarkable ER effects.[5, 6] However, the high cost of LCP is a serious problem for its industrialization. We have focused on copolymers having hard segments and flexible chains, which can be easily prepared from conventional materials. The copolymers can exhibit unique characteristics due to the complicated segmental behaviors, which generates potentially useful functions. Here we demonstrate a unique electrical property of a polyether-polycarbamate solution as a novel ER material.

A polyether-polycarbamate copolymer was prepared by condensation of corresponding polyether and diisocyanate according to literature.[7] A mixture of polypropylene glycol ($\overline{Mw}$ = 3000) and 4,4'-diphenylmethane diisocyanate at the molar ratio of 1:2 was stirred for 3 h at 80-85 ℃ in the presence of Sn catalyst. Methanol was added to the obtained copolymer ($\overline{Mw}$ = 3500) to modify the terminal isocyanate groups into methoxyl groups. The resulting copolymer was diluted with polypropylene glycol ($\overline{Mw}$ = 3000) at the molar ratio of 1:1. The final solution contained 7 wt% hard-segment due to the carbamate and diphenylmethane residues. Shear viscosity and dynamic viscoelasticity were measured under a constant DC electric field ranging between 0 and 3 kV/mm by using a modified Couette type rheometer [8] (Rheology Co. Ltd., MR-300 V2) at room temperature.

Figure 1 shows the effect of electric field strength on the shear viscosity η at various shear rates $\dot{\gamma}$. It is found that the viscosity decreases with increasing field strength, particularly at low shear-rate region. Under each condition, the initial viscosity was recovered immediately after the electric field was removed. This reversible decrease of viscosity induced by electric field is opposite to the usual ER effect. The viscosity

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decrease tended to saturate when the field strength exceeded 3 kV/mm. Further increase of field strength resulted in electro-conduction which inactivates the ER effect. Figure 2 shows the storage modulus G' plotted against angular velocity ω of the sinusoidal shear strain. At low ω region, G' drastically decreases with increasing strength of electric field. The decrease of G' under an electric field is also opposite to general behavior of ER fluids. This phenomenon characterizes the negative ER effect as well as the decrease of viscosity.

It should be noted that the negative ER effect appears only at low shear-rate conditions, which is a distinguished feature of the present polymeric fluid from other homogeneous ER fluids such as LCP. We will explain the different shear-rate dependence from a comparison of the possible mechanisms for these ER effects. In the case of LCP the electric field induces a network structure which gives the fluid a rubber-like elasticity.6) On the other hand, the ER effect in the present fluid is supposed to be governed by an electrically induced phase-separation. The hard segments in the copolymer can aggregate under an electric field, and the segmental domains are less effective to resist against shear deformation. Consequently the fluidity under a strong electric field depends mostly on the nature of the soft-segments and/or of the solvent. This interpretation is consistent with the shear-rate dependence because the phase-separated structure is perturbed by the intense shear deformation under high shear-rate conditions. It is easily understandable that the randomized phase-structure is similar to that under no electric field. Further experiments are in progress to confirm the phase structure under an electric field.

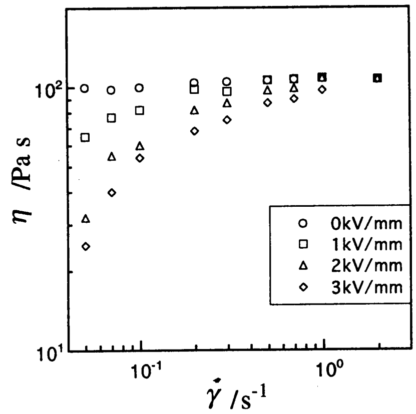

Fig. 1. Shear viscosity vs. shear rate under various DC fields.

The negative ER effect enables us to control the rheological properties of fluids to a great extent. This effect provides us a new concept for various applications of ER fluids from the viewpoint of regulation of the 'positive and negative ER effects' by changing the molecular structure.

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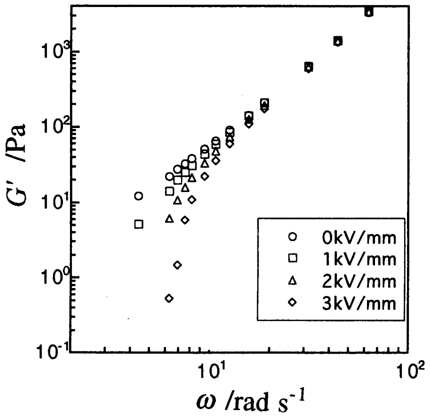

Fig. 2. Dependence of storage modulus on the angular velocity under various DC fields.

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