

Ultrasonic Disassociation of EVA Random Copolymer in Dilute Solutions

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ABSTRACT: Ultrasonic disassociation of the ethylene–vinyl acetate (EVA) random copolymer in 1,2-dichloroethane (DCE), cyclohexane (CYH), and their solvent mixtures was investigated using viscometry and dynamic laser light scattering (DLS). It was found that the disassociation of the EVA aggregates in solutions increases with increasing the time and intensity of ultrasonic shearing and approaches invariant finally. This phenomenon is especially marked for the EVA copolymer with low vinyl acetate (VA) content in the polar solvent of DCE at higher concentration and lower temperature. This is attributed to disassociation of the ethylene segment of the EVA random copolymer in dilute solutions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2798–2802, 2001

Key words: ultrasonic disassociation; EVA copolymer; polymer solution

INTRODUCTION

EVA random copolymers are versatile polymers that have a broad range of applications¹ due to their variation, significantly in their chemical and physical properties with their composition and extra conditions. One of the important applications for EVA copolymer and its derivatives is as a polymer flow improver of crude oil and its product.² The effects of the structures and the molecular parameters of the EVA copolymers on flowability of the oil have been studied.^{3–5} Recently, the association behavior of the EVA flow improver in dilute solutions was investigated and affected by solvent properties, EVA concentration, solu-

tion temperature, heat history of the solution, the VA content of the EVA copolymer, etc.^{6,7} Interestingly, it was found the rheological behavior of oil doped with an EVA flow improver such as the pour-point depression and viscosity reduction are influenced by the association of EVA copolymer in solution.^{8,9} The aggregated state of EVA chain in oil or wax solution is favorable to the rheological behavior of the systems, but the flowability of the oil doped the flow improver commonly becomes worse after pump shearing in the pipeline. The reasons for the reduction of the flowability, degradation, or disassociation of the polymer flow improver are not clear. Peiffer et al.^{10,11} have even reported shear dependent rheology of ionomer solution in detail; shear thickening and shear thinning were observed due to association and disassociation of the ionomer. Ultrasonic degradation of the polymer in solution can also be found elsewhere.^{12,13} Also, the ultrasonic technique is a popular method to study the compatibility or mis-

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cibility of polymer blends in solution,^{15,16} but the study of ultrasonic disassociation of polymer in solution is limited. In this study, we give the verification of disassociation of the EVA copolymer in dilute solutions by the ultrasonic technique, and further investigate the ultrasonic effect of the association of EVA copolymer in dilute solutions by viscometry and dynamic laser light scatter.

EXPERIMENTAL

Sample

The two EVA samples (EVA₃₀ and EVA₃₈) used were from the Chemical Engineering Institute of Shanghai. Their number-average molecular weights (16,900, 16,800), molecular weight distributions (2.18, 1.96), and vinyl acetate contents (30, 38 wt %) were characterized using a Knauer membrane osmometer, a Waters 150C SEC, and a Carlo Erba-1106 element analyzer, respectively.

Preparation of EVA Solution

EVA samples were dissolved in DCE, CYH or DCE/CYH thoroughly at 45°C and then clarified by Millipore filter. The solution after the clarification was reheated to 45°C and maintained for about 30 min and then quenched from 45 to 0°C and kept at 0°C for 30 min before being reheated to a higher measurement temperature. The ultrasonic shearing of the sample solutions in viscometer was conducted using CQ250 Ultrasonic Washing of Shanghai Ultrasonic Instrument Company at the designated temperature.

Viscometry

Viscosity measurement of the solutions was made with an Ubbelohde viscometer at the designated temperature with deviation of $\pm 0.02^\circ\text{C}$. Reproducibility of the efflux time was within 0.1 s. Intrinsic viscosities $[\eta]$ were determined by one-point method using an equation⁶

$$[\eta] = \frac{\eta_{sp}}{c \sqrt{\eta_r}}$$

Laser Light Scattering (LLS)

A commercial LLS spectrometer (Brookhaven BI9000AT equipped with a BI200SM correlator) was used with an argon ion laser (Innova 300,

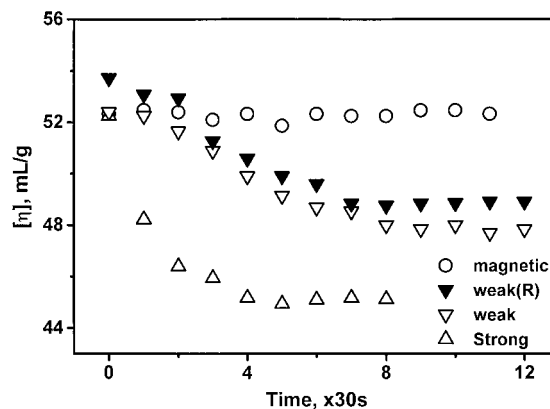


Figure 1 The variation of $[\eta]$ of the EVA₃₀ sample with the time of ultrasonic shearing (TUS) in DCE solvent at a concentration of 0.002 g/mL at 23°C, where the up triangle and down triangle symbols represent the strong and weak intensity of ultrasonic shearing, respectively, and the circle symbol represents the magnetic stir for the solution.

output power is ~ 1 w at $\lambda = 514.4$ nm) as the light source. Dynamic LLS experiments with 90° angle were carried out at $23.0 \pm 0.1^\circ\text{C}$. The translational diffusion coefficient D_T and the hydrodynamic radius R_h were obtained from the average decay rate Γ and Stokes-Einstein formula $D_T = \Gamma/q^2$, $R_h = kT/6 \pi \eta D_T$, where the scattering vector $q = \pi n/\lambda \sin(\theta/2)$ with θ , λ , k , T , η , and n being the scattering angle, the incident wavelength in vacuum, Boltzmann constant, absolute temperature, solvent viscosity, and solvent refractive index, respectively.

RESULTS AND DISCUSSION

Ultrasonic Disassociation Phenomenon

Figure 1 shows the variation of $[\eta]$ of EVA₃₀ sample with the time of ultrasonic shearing (TUS) in DCE solvent at concentration of 0.002 g/mL at 23°C, where the $[\eta]$ presents the size of polymer coil, and the up triangle and down triangle symbols represent strong and weak intensity of ultrasonic shearing, respectively. It is clear that the $[\eta]$ values decrease rapidly at the beginning and then leave off with the TUS regardless of strong or weak ultrasonic intensity, but the $[\eta]_{si}$, which presents the $[\eta]$ that is invariant with the TUS, is much larger in weak ultrasonic shearing compared to that in strong ultrasonic shearing, and also, the TUS for $[\eta]_{si}$ is longer in weak ultrasonic shearing than in strong ultrasonic shearing. The

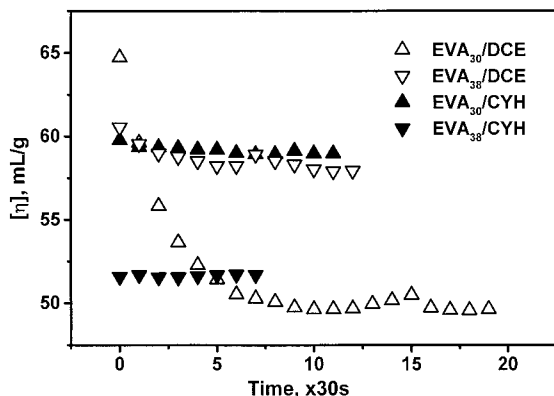


Figure 2 The variation of $[\eta]$ of the EVA₃₀ and EVA₃₈ samples with the TUS in DCE and CYH solvents, respectively, at $C = 0.01$ g/mL at 23°C.

$[\eta]$ values, however, are independent on the time of the magnetic stir at all (circle symbol in Fig. 1), which was from our previous work.¹⁷

Ultrasonic irradiation is a procedure commonly used to break up polymer chain in solution.¹² The curve with (\blacktriangledown) symbol is a repeated curve of the curve with (∇) symbol in Figure 1 after the solution sample was reheated from 23 to 45°C and kept at 45°C for 1 h. Both curves are almost same, so it means that the $[\eta]$ values that decreased with the TUS is not caused by the ultrasonic degradation of the EVA chains. Therefore, we believe that $[\eta]$ reduction with TUS is due to ultrasonic disassociation of EVA chains in solution.

VA Content and Solvent Effects of Ultrasonic Disassociation

Figure 2 shows the variation of $[\eta]$ of EVA₃₀ and EVA₃₈ samples with the TUS in DCE and CYH solvents, respectively, at $C = 0.01$ g/mL at 23°C. A decreasing of $[\eta]$ with increasing the TUS reveals dramatically for EVA₃₀ more than for EVA₃₈ in DCE solvent, and finally a very lower $[\eta]_{si}$ value is displayed for the EVA₃₀ sample compared to that of the EVA₃₈ sample. This means that the solvent DCE is poorer for EVA₃₀ than for EVA₃₈ according to their $[\eta]_{si}$ values, but the $[\eta]$ (before the ultrasonic shearing, marked $[\eta]_{s0}$) of EVA₃₀ in DCE is larger than that of EVA₃₈ in DCE. Therefore, the association of EVA₃₀ in DCE is greater than that of EVA₃₈ in DCE. This means the association of EVA in DCE comes from ethylene segments in EVA macromolecules. So, the more ethylene segments, the larger aggregation in EVA macromolecules; this is the same as that

in the association of EPDM molecules.¹⁸ The aggregation of ethylene segments, however, is not resistant to the TUS. Oppositely, a very few decreasing of $[\eta]$ of EVA₃₀ and EVA₃₈ in CYH with TUS is seen in Figure 2; the reason will be discussed later.

Figure 3 shows the variation of $[\eta]$ of EVA₃₀ in DCE with the composition of DCE/CYH solvent mixture at $C = 0.01$ g/mL at 23°C, where $[\eta]_{s0}$ and $[\eta]_{si}$ represent the $[\eta]$ of EVA₃₀ before ultrasonic shearing and after ultrasonic shearing to invariant, respectively, and Φ_c is the volume fraction of CYH in the solvent mixture. From Figure 3 it can be seen that both $[\eta]_{s0}$ (circle) and $[\eta]_{si}$ (triangle) of EVA₃₀ increase then decrease with Φ_c , but they have almost same value when $\Phi_c = 0.4$. This means that the ultrasonic effect decreases with increasing of Φ_c and disappeared at about $\Phi_c = 0.4$. According to the same maximum of $[\eta]_{s0}$ or $[\eta]_{si}$ at about $\Phi_c = 0.7$, it indicates that the solvent mixture at the composition of $\Phi_c = 0.7$ is the cosolvent for EVA₃₀, i.e., it is a better solvent than the solvent DCE and CYH, respectively. In other words, association of EVA₃₀ exists in both solvent DCE and CYH, but they are two different types of association, ethylene segment association, and VA segment association, respectively, because both solvents are selective solvents for EVA copolymer, DCE is a good solvent for the VA segment and a nonsolvent for the ethylene segment and vice versa for CYH solvent. And the former is sensitive to ultrasonic effect and the latter is independent on ultrasonic shearing according to the difference between $[\eta]_{s0}$ and $[\eta]_{si}$. That is to say,

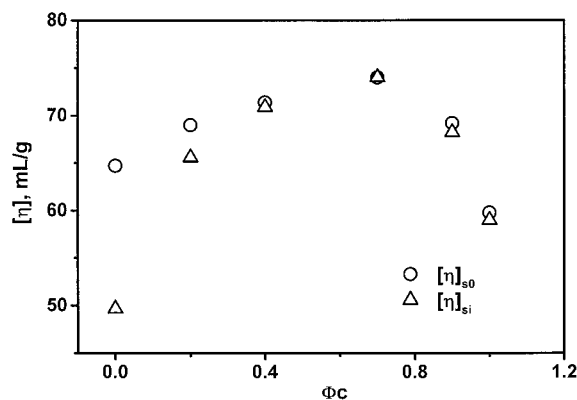


Figure 3 The variation of $[\eta]$ of EVA₃₀ in DCE with the composition of DCE/CYH solvent mixtures at $C = 0.01$ g/mL at 23°C, where $[\eta]_{s0}$ and $[\eta]_{si}$ represent the $[\eta]$ of EVA₃₀ before and after ultrasonic shearing to the invariant, respectively, and Φ_c is the volume fraction of CYH in solvent mixtures.

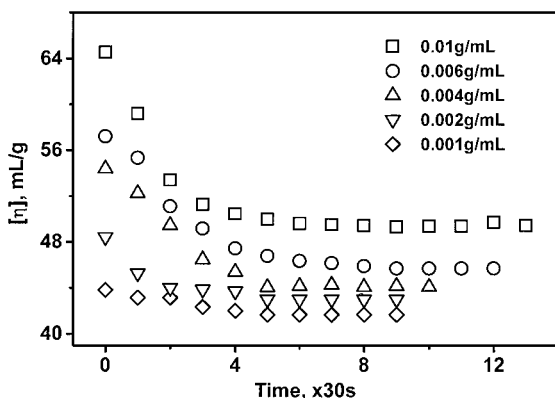


Figure 4 The variation of $[\eta]$ of EVA₃₀ with the TUS in DCE for various EVA₃₀ concentrations from $C = 0.01$ g/mL to 0.001 g/mL at 23°C .

ultrasonic disassociation is dependent on the types of the association of the EVA molecules. It is somewhat similar to the case that the association of a lightly sulfonated polystyrene ionomer solution caused by the mechanical shearing depends on the types of the solvent such as a nonpolar solvent or higher dielectric constant solvent.^{10,11}

Concentration and Temperature Effect of Ultrasonic Disassociation

Figure 4 shows the variation of $[\eta]$ of EVA₃₀ with the TUS in DCE for various EVA₃₀ concentrations from $C = 0.01$ g/mL to 0.001 g/mL at 23°C . Clearly, great ultrasonic effect occurs at high EVA concentration because of a larger association in a higher concentration. At about $C = 0.001$ g/mL, almost no association of this system at 23°C shows; this concentration is a little lower compared with the critical association concentration of $C_A = 0.003$ g/mL in the same system at 25°C , which was estimated by $\eta_{sp}/C \sim C$ or $[\eta] \sim T$ method;⁶ this difference is caused by different temperature or/and different methods for assessment of C_A .

Figure 5 shows the variation of $[\eta]$ of EVA₃₀ in DCE with the TUS at various temperatures. The lower the temperature, the larger the ultrasonic disassociation due to much more ethylene segment association at low temperature. At about 45°C , the $[\eta]_{si}$ equals to $[\eta]_{s0}$ for this solution sample with a concentration of $C = 0.01$ g/mL. Another two solution samples with a concentration of $C = 0.005$ g/mL and 0.002 g/mL were done; their temperatures were 40 and 35°C , respectively, at which the $[\eta]_{s0} = [\eta]_{si}$, i.e., no ultrasonic

effect exists. In other words, reducing the concentration and rising the temperature is equivalent to removing the association of EVA in the dilute solution of DCE by ultrasonic shearing. In addition, the curve of $[\eta]$ vs. the TUS at the same temperature, especially at lower temperature, is similar to the curve of $[\eta]$ vs. T , i.e., the $[\eta]$ values decrease rapidly, then leave off either with the increasing of the TUS at same temperature (see curve \diamond in Fig. 5) or with the increasing of the solution temperature without ultrasonic shearing (see curve \blacklozenge in Fig. 5). That is to say, it is possible to control the association of EVA in dilute solutions through changing the temperature or the TUS for the solutions.

Ultrasonic Effect of $\langle R_h \rangle_{app}$ and Its Stability

Figure 6 shows the apparent average hydrodynamic radius $\langle R_h \rangle_{app}$ of EVA₃₀ aggregates with the TUS in DCE at $C = 0.01$ g/mL at 23°C . As the variation of $[\eta]$ in viscometry, $\langle R_h \rangle_{app}$ values from DLLS also decrease dramatically, then gradually and leave off ($\langle R_h \rangle_{app,si} \cong 150$ nm) finally with the increasing of the TUS. According to the large value of $\langle R_h \rangle_{app,si}$, however, the EVA aggregates still exist under the ultrasonic intensity used. The $\langle R_h \rangle_{app,si}$ is independent on the storage time at 23°C , and no changing of $\langle R_h \rangle_{app}$ demonstrates after storage for 2 days, seeing the symbol (\bullet) in Figure 6. This result is in very good agreement with that from viscometry, i.e., $[\eta]_{si}$ keeps invariant after a storage time of 54 h at 23°C . This indicates that the solutions are stable after being sheared to $[\eta]_{si}$ or $\langle R_h \rangle_{app,si}$.

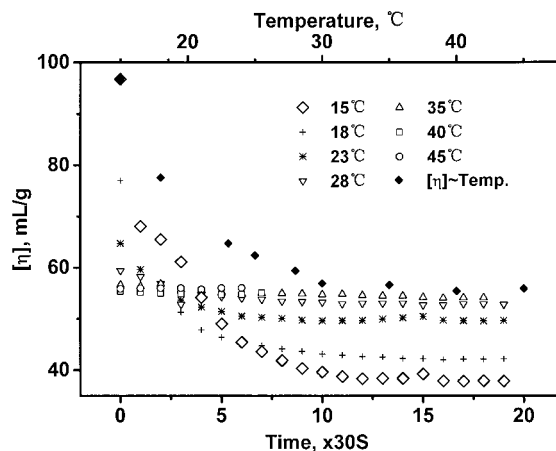


Figure 5 The variation of $[\eta]$ of EVA₃₀ in DCE with the TUS at various temperatures or with temperature without ultrasonic shearing (\blacklozenge symbol).

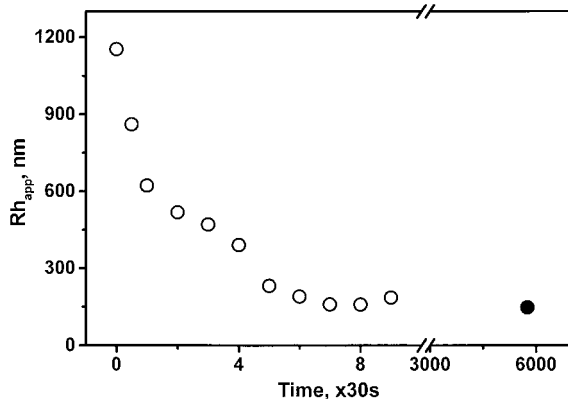


Figure 6 The apparent average hydrodynamic radius $\langle R_h \rangle_{app}$ of EVA₃₀ aggregates with the TUS in DCE at $C = 0.01$ g/mL at 23°C.

CONCLUSIONS

The coil dimensions of EVA copolymer, $[\eta]$ or $\langle R_h \rangle_{app}$, in the DCE solvent decrease dramatically with the increasing of the TUS; this is not caused by the ultrasonic degradation, but by the ultrasonic disassociation. Ultrasonic shearing is very effective to the disassociation of ethylene segment association in the EVA copolymer in the DCE solvent compared with that of the VA segment association in the EVA copolymer in the CYH solvent. Prolonging the TUS for a solution at the same temperature could be very similar with the rising solution temperature without ultrasonic shearing for the disassociation of EVA aggregates. The coil dimensions of EVA aggregates, irrespective of $[\eta]_{si}$ or $\langle R_h \rangle_{app,si}$, which are invariant with the TUS at some intensity of ultrasonic shearing, are resistance to storage at the same temperature. The ultrasonic technique is also a useful method to change the coil dimension of EVA aggregates in dilute solutions besides the solvent, temperature, and concentration of the solutions.

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