Association of Ethylene Vinyl Acetate Copolymer in Dilute Solutions. V. Stability and Pour Point Depression to Wax Solutions

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ABSTRACT: The stability of two kinds of aggregation states of ethylene vinyl acetate (EVA) copolymer in dilute solution of 1,2-dichloroethane has been investigated by viscometry. It was found that good storage-time, shearing, and dilution resistance were displayed for both states of EVA molecule with intra- and interchain association. And for the pour point depression of wax solution doped with EVA, the EVA in intrachain aggregation state was better than the EVA in interchain aggregation state. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 836–841, 2000

Key words: polymer solution; association; EVA; pour point depressant and viscometry

INTRODUCTION

EVA random copolymers are well known as pour point depressant of crude oil and its products.[1,2] However, like other pour point depressants the regularity and the mechanism of the pour point depression of oils doped with EVA are not too clear up to now. We have found that the efficiency of EVA as pour point depressant was dependent on solvent property.[3] Recently,[4,5] the association behaviors of EVA copolymer in dilute solution of 1,2-dichloroethane (DCE) and cyclohexane (CYH) were reported. Two kinds of association states of EVA in DCE exist: one was called intrachain association, which was formed by a fast-cooling thermal process; the other was called interchain association, which was formed by a slow-cooling thermal process. According to the dynamic light scatter result[6] the intra- and interchain associa-tion of EVA molecules represent the individual collapsed chain aggregation and microgel-like aggregation, respectively. According to the changing of the slope in $\eta_{sp}/c \sim c$ curve of EVA in dilute solution, a critical association concentration, C_A, was proposed,[7] at which a transition between intra- and interchain association demonstrates, and the solvent mixture effect of EVA solution on C_A was studied in detail.[8] In this article, the stability of both aggregation states of EVA in dilute solution was approached. Also their pour point depression for wax solution was examined.

EXPERIMENTAL

Material and Characteristic

Three types of commercial of EVA samples (designated as A, B, C) were used. Samples C_1, C_2, and C_3 were prepared by fractionation from 1% benzene solution of sample C, with isopropanol as precipitant.[9] Fractionation was carried out at 30.00 ± 0.02 °C. M_n, VA content of five samples A ($M_n = 1.69 \times 10^4$, VA = 29.7%), B ($M_n = 1.68$
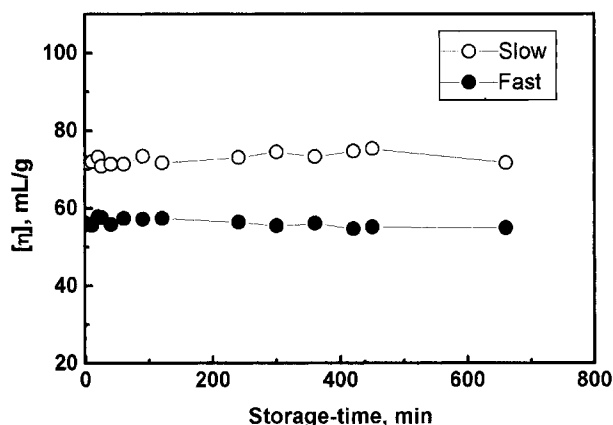
Figure 1 Relation between $[\eta]$ and storage-time for sample EVA-A in DCE with fast and slow-cooling thermal processes, respectively, at 15°C.

$\times$ 10^4, VA = 37.5%), C_1 (M_n = 3.15 $\times$1 0^4, VA = 32.7%), C_2 (M_n = 2.72 $\times$ 10^4, VA = 31.1%), C_3 (M_n = 1.25 $\times$ 10^4, VA = 31.5%) were characterized by Knauer VPO instrument and Carlo Erba 1106 element analyzer, respectively. The wax was supplied by the institute of the refined oil company in Hangzhou and purified by petroleum ether, which is normal paraffin with a melting temperature of 49.4°C estimated from differential scanning calorimetric (DSC) measurements. All additives used are of reagent grade, except for the surfactants, which are of chemical grade.

Solution Preparation

There are two kinds of thermal histories in preparing EVA solution except as mentioned in text. One is a fast-cooling process in which the EVA solutions are fast quenched from 45 to 2°C (ice water) and are kept at 2°C for 15 min before being reheated to a higher measurement temperature. The other is a slow-cooling process in which the EVA solutions are gradually cooled from 45 to 15°C over 6 h and then are kept at 15°C for about 6 h before a final quenching from 15 to 2°C and then kept at 2°C for 15 min.

Efflux-Time and Intrinsic Viscosity Measurement

Efflux-time measurement of the solutions was conducted with an Ubbelohde viscometer at definite temperature with deviation of ± 0.02°C. The reproducibility of efflux-time was of 0.05 sec. The intrinsic viscosity, $[\eta]$, value of EVA copolymer at different storage-time or shearing number was calculated by the one-point $[\eta]$ equation,[10]

$$[\eta] = \frac{\eta_{sp}}{cx \sqrt{\eta_r}} \qquad (1)$$

which is suitable for polymer/solvent systems with larger Huggins constant, usually K' > 0.5.

Pour Point Measurement

The pour points of various wax solutions with or without doped EVA were detected by a BLY thermoelectric cooling freezing pour point tester. The cooling temperature of the tester was regulated at about −30°C.

RESULTS AND DISCUSSION

Stability of Intra- and Interchain Association

Storage-Time Resistance

Figure 1 shows a typical storage-time dependence of $[\eta]$ of sample EVA-A aggregates in DCE with the concentration of 0.002g/mL at 15°C, where the filled and hollow symbols represent the solutions treated using the fast- and slow-cooling thermal processes, respectively. The $[\eta]$ of EVA-A in both of the fast and slow-cooling processes are about 56 mL/g and 72 mL/g, respectively. The different values are a result of the intra- and interchain association of EVA molecules in solutions because of different thermal processes used. The $[\eta]$ in each case is independent on the storage-time. This indicates that these two kinds of aggregates have good stability for the storage-
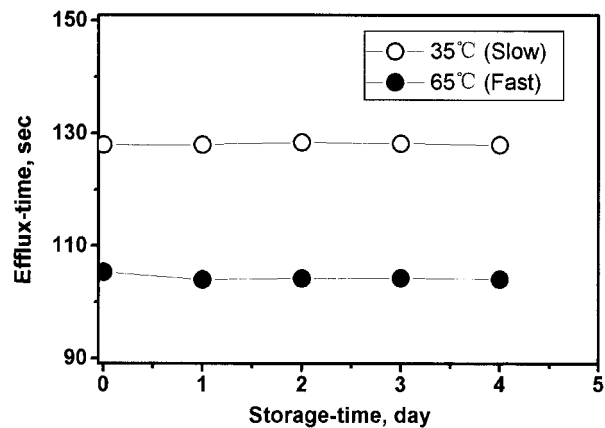

Figure 2 Relation between efflux-time and shortage time for sample EVA-A in DCE at 20 °C with dissolving temperature of 35°C (slow cooling) and 65°C (fast cooling), respectively.
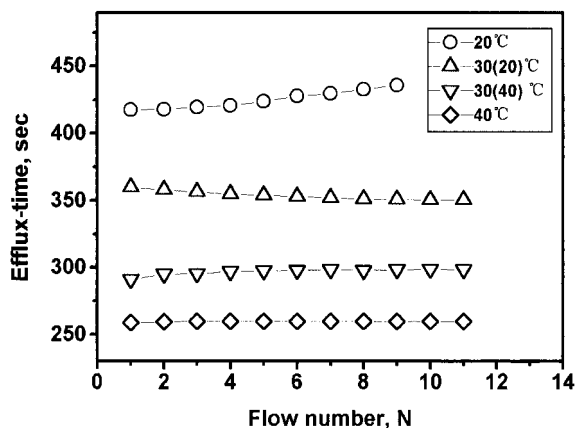
Figure 3 Relation between efflux-time and flow number for sample EVA-A in DCE at different temperature with different thermal history.

time of 11 h. Figure 2 shows the storage-time dependence of the efflux-time, in the Ubbelohde viscometer, of the EVA-A solution in DCE with the concentration of 0.0046 g/mL at 20°C. The solution 1 (hollow symbol) was prepared at 35 °C and then cooled from 35°C to 20°C. The solution 2 (filled symbol) came from solution 1, but reheated to 65°C and maintained at 65°C for half hour, finally cooled from 65 °C to 20 °C. It can be seen that the lower dissolving temperature of 35 °C (close to slow-cooling process) makes solution 1 have larger efflux-time or $[\eta]$, that is, interchain association. The higher dissolving temperature of 65°C (close to fast-cooling process) makes solution 2 have smaller efflux-time or $[\eta]$, that is, intrachain association. However, the efflux-time in both cases is independent of the storage-time even up to 96 h. Again, this indicates that both aggregates have enough stability.

Shearing Resistance

Polymer chains in solution or melt are always sheared when they flow. Figure 3 shows the flow (or shearing) number, N, through the capillary, dependence of the efflux-time of EVA-A solution of DCE with concentration of 0.00918 g/mL in the capillary of an Ubbelohde viscometer at 20, 30(20), 30(40), and 40°C, respectively. The solutions at 30(20)°C and 30(40)°C mean that there are two kinds of different solutions at the same temperature of 30°C, but, they came from the solutions at 20°C (i.e., low dissolving temperature) and at 40°C (i.e., high dissolving temperature), respectively. In this experiment, only one

solution was used to determine the efflux-time at different temperatures in 20, 30(20), 40, and 30(40)°C order. It is interesting to see that a large difference of the efflux-time between the solutions at 30(20)°C and 30(40)°C, about 50 sec, was displayed. This means that two kinds of states of EVA chains exist at the same temperature of 30°C [30(20)°C and 30(40)°C], that is, inter- and intrachain association at 30(20)°C and 30(40)°C, respectively. These states are almost stable with flow shearing.

Figure 4 gives a magnetic stir number, N, dependence of the $[\eta]$ of EVA-A in DCE with concentration of 0.002 g/mL at 23 °C. The solution was treated in fast-cooling process, and each vigorous agitation maintained for 1 min. Apparently, agitation effect on the size of EVA molecule was not displayed with increasing of the stir number, so, it is very stable to agitation shearing.

Dilution Resistance

Figure 5 shows concentration dependence of the reduced viscosity, η_{sp}/c of EVA-A in DCE at 15 °C, where the filled and hollow symbols represent the EVA-A solutions treated in fast and slow-cooling processes, respectively. Obviously, no superposition approach of these two curves, $\eta_{sp}/c{\sim}c$, can be seen within experimental concentration range, this means that these two kinds of associations have good dilution resistance. But, the stability of the intrachain association is better than that of the interchain association because the former's $\eta_{sp}/c{\sim}c$ curve (solid symbols) is almost a straight line, and the latter's $\eta_{sp}/c{\sim}c$ cure (hollow sym-
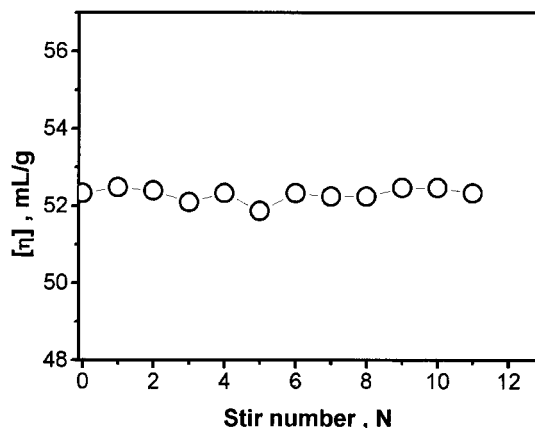

Figure 4 Relation between $[\eta]$ and stir number for sample EVA-A in DCE with fast-cooling thermal process at 23°C.
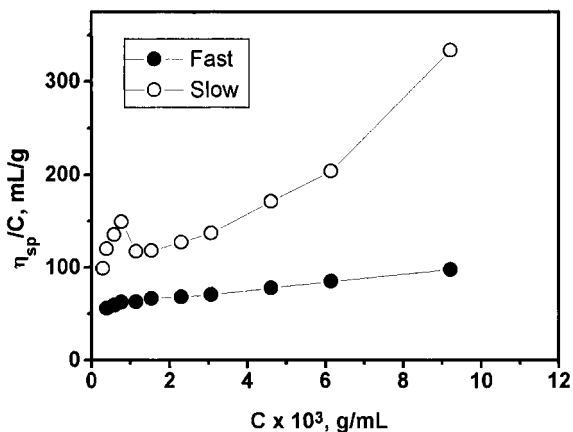
Figure 5 Variation of η_{sp}/c with c for sample EVA-A in DCE with fast- and slow-cooling thermal process, respectively, at 15°C.

Figure 6 EVA-A dosage dependence of ΔT_{pp} of DCE containing 1.5 (wt) % wax with and without EVA-A pour point depressant, which was treated in fast and slow-cooling thermal processes, respectively.

bols) is nonlinear. The upturn of the $\eta_{sp}/c \sim c$ curve in concentrated solution region indicates the increasing of the aggregation number of the polymer molecule in solution.[11,12] The discontinuation of the $\eta_{sp}/c \sim c$ in dilute solution region represents a transition between inter- and intrachain association[7,8,13,14] or a incipient overlap of polymer coils in dilute solution.[15]

Pour Point Depression

Figure 6 shows the EVA-A dosage dependence of the change of pour point, ΔT_{pp}, of DCE containing 1.5 (wt) % wax with and without EVA-A pour point depressant, where the filled and hollow symbols represent the EVA-A solutions, with concentration of 0.002g/mL, treated in fast- and slow-cooling processes, respectively. In spite of EVA-A dosage, the EVA solution treated in fast-cooling process displays better pour point depression than the EVA solution treated in slow-cooling process, that is to say, intrachain association of EVA molecule is favorable for pour point depression of wax solution, compared the interchain association of EVA molecule. It must be pointed out that the wax solution doped with EVA solution should not be heated beyond 35°C in the pour point measurement in order to keep the different aggregation states of EVA chains from being destroyed.[6]

Figure 7 again shows the concentration effect of EVA-A parent solution on ΔT_{pp} of DCE containing 2.5 (wt) % wax with and without 50 ppm EVA-A, where filled and hollow symbols represent EVA solutions treated in fast and slow-cool-
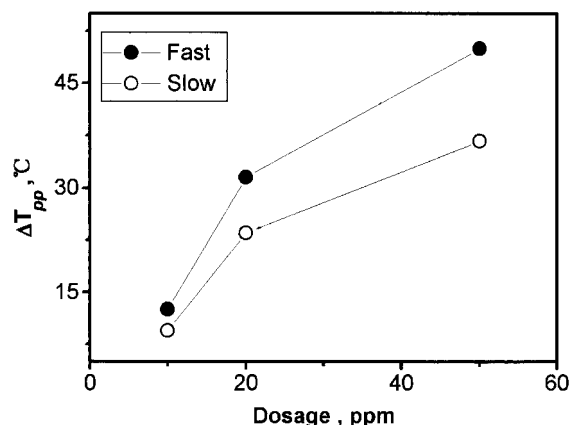
ing processes, respectively. It gives us the same result as in Figure 6, viz., the EVA parent solution treated in the fast-cooling process, in which the EVA molecule reveals intrachain association mostly, has better pour point depression. Besides, for both of the parent EVA solutions, their pour point depression gets worse with the increasing of the concentration of the parent EVA solution. This is because there are much more interchain association in more concentrated EVA solution.

The critical association concentration, C_A, effect of EVA in DCE-CYH solvent mixture with additives on pour point depression of various wax solutions is given in Table I, and the C_A effect of
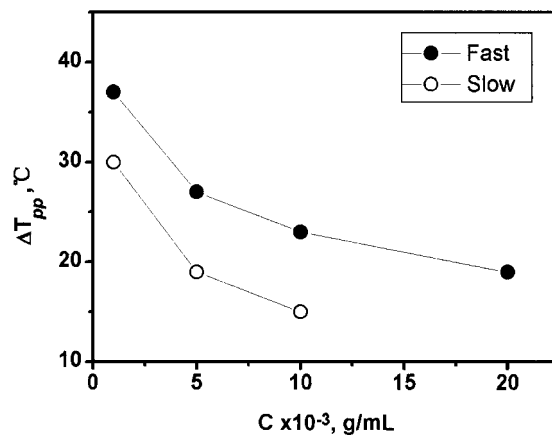

Figure 7 Concentration effect of EVA-A parent solution on ΔT_{pp} of DCE containing 2.5 (wt) % wax with and without 50 ppm EVA-A, which was treated in fast and slow-cooling thermal processes, respectively.

Table I C_A **Dependence of** ΔT_{pp} **of Wax Solutions with and without EVA-B [solvent: DCE/CYH = 7V/3V, wax: 10 (wt) %]**

Additive Name	Amount (ppm)	$C_A \times 10^3$ (30°C) (g/mL)	ΔT_{pp} (°C)	Dosage of EVA-B (ppm)
–	–	2.3	15	50
Ethanol	3000	4.1	28	50
Acetic acid	3000	3.8	25	50
Butanol	3000	3.8	25	50
Heptanic acid	3000	3.3	18	50
Dodecanol	3000	2.6	17	50
Dodecanic acid	3000	1.8	14	50
Octadecanol	3000	1.7	13	50
Octadecaic acid	3000	1.3	12	50
Ethanol	3000	4.1	30	75
Ethanol	1000	2.5	22	75
Ethanol	500	2.0	19	75
Span80	5000	1.24	31.5	100
Span80	3000	1.6	36	100
Span80	1000	1.95	45	100
Octadecanic acid	3000	1.3	33	100
Octadecanol	3000	1.7	43	100
Octadecanic amine	3000	3.36	50	100
–	–	2.3	47	100

EVA with different molecular weight in DCE on pour point depression of wax solution is given in Table II. From both Tables I and II, it can be clearly seen that in each group, the higher the C_A, the larger the ΔT_{pp}. This is because C_A is a transition concentration between intra- and interchain association,[7,8,13,14] so, the EVA solution with higher C_A value represents stronger intrachain association or weaker interchain association of the EVA molecules at the same temperature. Again, it leads us to consider that intrachain association of EVA is better than interchain association for pour point depression of the wax solution. This is probably due to having much more interaction between wax and EVA in the intrachain association state than in the interchain association state according to polymer-flow interaction.[16]

CONCLUSIONS

The dimension of EVA copolymer molecule in dilute solution of 1,2-dichloroethane is dependent on the thermal history of solution preparation. The smaller dimensions of the EVA macromole-

Table II C_A **Dependence of** ΔT_{pp} **of Wax Solutions with and without EVA-C [solvent: DCE, wax: 5 (wt) %]**

Sample	EVA-C Pour Point Depressant			$C_A \times 10^3$ (25°C) (g/mL)	ΔT_{pp} (°C)
	$M \times 10^{-4}$ (g/mol)	VA Content (wt) %	Dosage (ppm)		
C_1	3.10	32.7	50	1.08	9
C_2	2.72	31.1	50	1.41	16
C_3	1.25	31.5	50	1.67	46

cules display when the EVA solutions are treated in a fast-cooling process or high-dissolving temperature, or vice versa, larger dimensions of the EVA macromolecules in the solution are given. These are caused by different association states of intra- and interchain. Both states have good resistance to storage-time, dilution and shearing of magnetic agitation, and flow in capillary. The EVA with intrachain association in solution offers more efficiency of pour point depression to wax solution than the EVA with interchain association in solution. The intrachain association of EVA in solutions can come from the EVA solution treated by a fast-cooling thermal process or from the EVA solutions with high C_A values, which are caused by addition of some additives such as ethanol.

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