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Conformational transition in (maleic anhydride mono-*n*-octyl itaconate) copolymer

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Summary

The dependence of intrinsic viscosity [η] on temperature for fractions of poly(maleic anhydride-co-mono-n-octylitaconate) [p(MA-co-MOI)] was studied. A discontinuity in [η] as function of temperature similar to that of poly(mono-n-octylitaconate) (PMOI) is found which has been attributed to a conformational transition of the polymer chain. This conformational transition can be removed by the addition of poly(dimethylsiloxane) (PDMS). The effect is interpreted in terms of interpolymer complexation.

Introduction

The discontinuity in the variation of intrinsic viscosity [η] against temperature has been reported by many authors (1-6). The observed discontinuity has been referred as a conformational transition. In this short communication we present viscometric results obtained with (p(MA-co-MOI), PDMS and their mixtures in tetrahydrofuran (THF) in dilute solution as function of temperature.

Experimental

Mono-n-octylitaconate synthesis and purification were described previously (7). Maleic anhydride was a commercial sample from Merck. Copolymerization was carried out by using α,α'-azobisisobutyronitrile (AIBN) as initiator at 336 K under N_2 atmosphere. Copolymer was fractionated by standard precipitation procedures using acetone as solvent and petroleum ether as precipitant. Molecular characterization was determined by Size Exclusion Chromatography (SEC) using a Perkin-Elmer High performance liquid chromatograph (HPLC) as described previously (8).

Viscosity measurements were carried out in THF at various temperatures with a Desreux-Bischoff dilution viscometer (9). Intrinsic viscosities [η] were determined by extrapolation to zero concentration of the reduced viscosity η_{sp}/c and inherent viscosity ln η_r/c according to usual procedures (10,11).

Results and Discussion

The intrinsic viscosity dependence on temperature for p(MA-co-MOI) fractions in THF is shown in Figure 1. All fractions show discontinuities in the viscosity in the range 278 to 303 K. This behaviour is similar to that obtained for PMOI in the same temperature range (7). No shifting in the discontinuity range is observed due to the presence of maleic anhydride units (see Figure 2).

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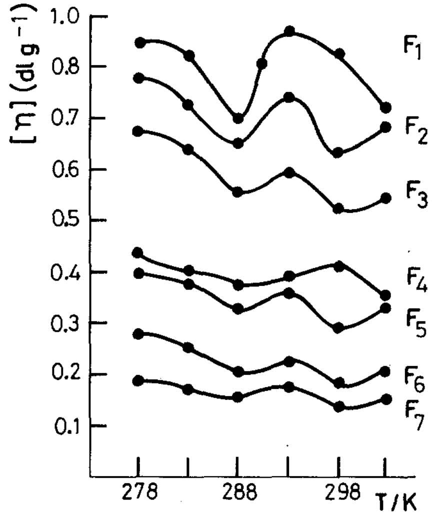

Figure 1. Variation of intrinsic viscosity [η] with temperature for fractions of p(MA-co-MOI) in THF.

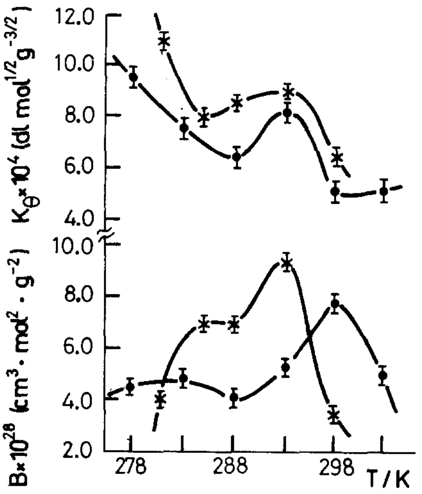

Figure 2. Variation of the conformational and thermodynamic parameters K_θ and B with temperature from Stockmayer-Fixman plots for × PMOI (Taken from ref 7); ● p(MA-co-MOI) in THF.

The discontinuity in the viscosity as function of temperature for PMOI have been interpreted in terms of conformational changes of the polymer chain (7). Therefore, it can be considered that p(MA-co-MOI) also undergoes a conformational transition at about 288 K. In order to clarify this behaviour it is necessary to know the unperturbed dimensions of the copolymer in THF at various temperatures. We have used one of the excluded volume theories, viz. the Stockmayer-Fixman (SF) method (12), to obtain K_θ. Figure 2 shows the variation of the unperturbed dimensions parameter K_θ and the thermodynamic parameter B also obtained from SF plots as a function of temperature for p(MA-co-MOI). In the same figure we have inserted the variation of K_θ and B for PMOI taken from ref. 7. As can be seen the homopolymer and the copolymer exhibit similar changes in K_θ and B between 278 and 298 K and a break point at 283 and 288 K for PMOI and p(MA-co-MOI) respectively. At the transition point one can observe a decrease of the unperturbed dimension of the polymers which means that the macromolecular coils become more compact. An attempt to obtain some evidence that the observed effect is probably due to the interaction of side groups of the polymer chain, we have studied the viscometric behaviour of mixtures of p(MA-co-MOI) with PDMS in dilute solution.

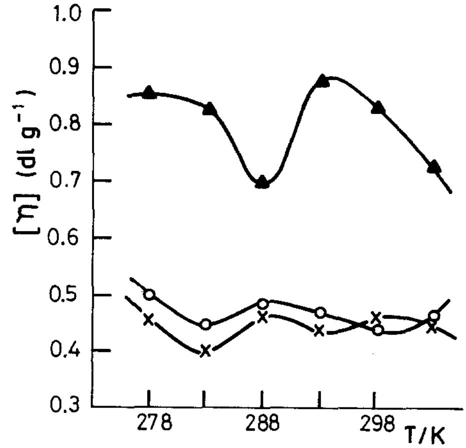

Figure 3. Variation of intrinsic viscosity [η] with temperature of ▲ p(MA-co-MOI); × PDMS; ○ mixture of PDMS with p(MA-co-MOI) in THF.

As can be observed in Figure 3, PDMS shows a rather smooth variation in [η] with temperature. The same figure ilustrates the viscosity-temperature curve for p(MA-co-MOI) when PDMS is added and it can be observed that the curve is flattened. This effect presumably could be due to the strong interaction between the oxygens of the main chain of PDMS and the carboxylic free group of the mono-n-alkylitaconate, similar to the effect found in blends of poly(monobenzylitaconate) with poly(ethylenoxide) in the solid state (13). The viscometric behaviour shown in Figure 3 are similar to those reported by Rashid et al. (14), for poly(methyl methacrylate) (PMMA) in carbon tetrachloride in the temperature range of 298 to 326 when poly(ethylene glycol) is added to PMMA solution.

The results suggest the formation of a possible soluble polymer complex (PC), because of the interaction between PDMS and p(MA-co-MOI). It is usually considered that the formation of a polymer complex can be observed viscosimetrically if the hydrodynamic volume of the complex is generally smaller than the sum of the hydrodynamic volumes of the individual components. Such a comparison can be performed through the gain concept (g) in viscosity (15), where:

$$g = \frac{(\eta_{sp})_{PC}}{(\eta_{sp})_{PDMS} + (\eta_{sp})_{p(MA\text{-}co\text{-}MOI)}}$$

and η_{sp} represents the specific viscosity of PC and the two polymers. g is less than 1 and therefore the polymer complex is very compact (Figure 3).

Considering these observations and those of Rashid's studies we could conclude that the complexation between the complementary polymers results in a more compact structure and causes conformational changes in the two polymer chains. These conformational changes are necessary to achieve the specific interaction to stabilize the complex.

The results and the tentative explanation we have presented, suggest that the conformational transition induced by temperature should be hindered by interpolymer complex formation.

Acknowledgements

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