lymerizations, will certainly find its place in describing systems with stronger nonspecific interactions.

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Diffusion and Surface Activity of Block Copolymers in Polystyrene Melts: Effects of Copolymer Molecular Weight and Morphology

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Several years ago, the time-dependent surface-tension changes in a polystyrene melt containing small amounts of surface-active styrene–dimethylsiloxane block copolymer were reported.[1] It was concluded that the early stages of adsorption were limited by diffusion of the block copolymer additive to the surface, and it was found that reasonable values of diffusion constants could be extracted from the data. During the course of that work, fragmentary results for some other copolymer additives were obtained but were not reported. In view of recent interest in diffusion in polymer melts and mixtures,[2,3] these results have been reexamined and are presented and discussed here.

Experimental Section

The styrene homopolymer used ($\bar{M}_n = 9290$) and all experimental procedures were the same as those previously described.[1] Two additional A-B block copolymers were used as additives: one had $\bar{M}_n$(osmotic) = 6800 and contained 14.6% Si (corresponding to styrene $(S)_{40}$–dimethylsiloxane $(D)_{36}$), while the other had $\bar{M}_n = 24\,200$ and contained 16.7% Si (S_{129}–D_{144}). In addition, a multiple sequence block polymer,[4] having the design structure $(D_{25}S_{50}D_{25})_x$, 16.0% Si, $\bar{M}_n = 69\,400$ (hence $\bar{x} = 7.8$), was used. Since these samples were not subjected to the fractionation applied to the earlier-described block polymer (S_{75}–D_{77}), it may be assumed that they were more polydisperse.

Results and Discussion

The experimental results are presented in Figures 1 and 2. According to our earlier analysis,[1] during the early stages of adsorption, while diffusion through the bulk is limiting the arrival of surfactant at the interface, the surface tension lowering is expected to be proportional to $t^{1/2}$. In the case of the three earliest points for the system containing the copolymer S_{129}–D_{144}, this relationship is obeyed. Accordingly, the diffusion constant can be estimated from the slope of a plot of $(\gamma_0 - \gamma)$ vs. $t^{1/2}$ (cf. eq 3 of ref 1) as 5.7×10^{-9} cm²/s, and this value has been used to construct the solid curve in Figure 1.

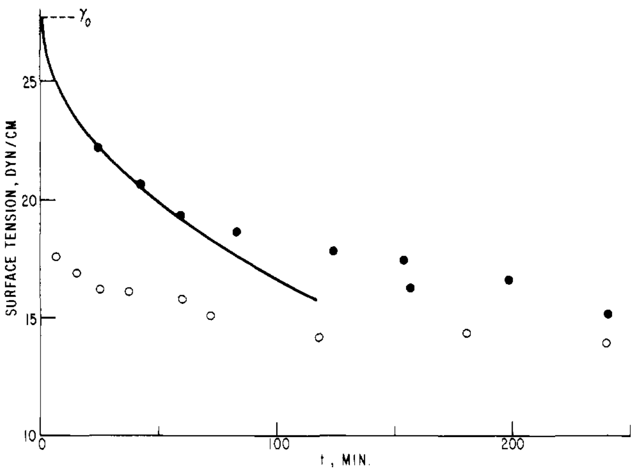

Figure 1. Surface tension at 200 °C as a function of time for blends of polystyrene with 0.1 wt % copolymer $S_{40}D_{36}$ (○) or $S_{129}D_{14}$ (●). The solid line is calculated for diffusion-controlled adsorption. γ_0 is the surface tension of polystyrene at 200 °C.

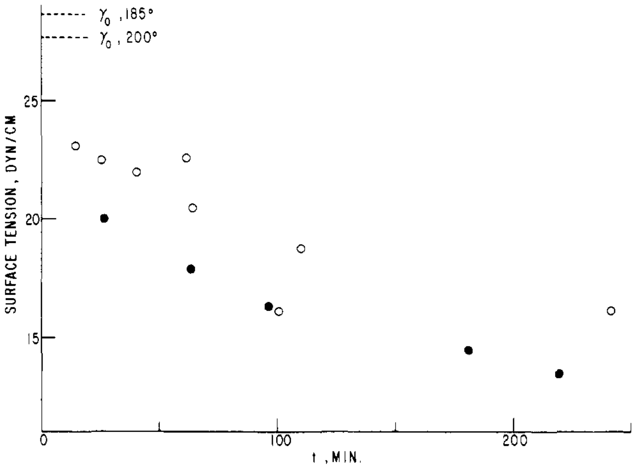

Figure 2. Surface tension of a blend of polystyrene plus 0.1 wt % copolymer $(D_{25}D_{50}D_{25})_{7.8}$ at 185 °C (○) and 200 °C (●). γ_0 is the surface tension of pure polystyrene at the indicated temperature.

Table I
Diffusion Constants for Block Copolymers in Polystyrene, Estimated from the Rate of Surface Tension Lowering

copolymer	T, °C	D, cm²/s
$S_{40}D_{36}$	200	$>5.3 \times 10^{-9}$
$S_{75}D_{77}$	200	3.6×10^{-8} [a]
$S_{129}D_{144}$	200	5.7×10^{-9}
$(D_{25}S_{50}D_{25})_{7.8}$	185	$>9.2 \times 10^{-8}$
	200	$>8.3 \times 10^{-8}$

[a] From ref 1.

Most of the data presented here pertain to the long-time slow approach to adsorption equilibrium, for which no detailed interpretation is available. However, since diffusion to the surface must precede adsorption, it is possible to use the earliest measured surface pressure value to estimate a lower limit for the diffusion constant. Values obtained in this way are listed in Table I. It must be recognized, of course, that these are lower limit values; there is no way to estimate from the present results how much larger the correct values are, and in fact they may be very much larger.

It is interesting to note that the multiple sequence block copolymer appears to have a diffusion constant substantially larger than those for the AB types. Since we have no information on the polydispersity of these samples, it is possible that this result merely reflects the presence of a low molecular weight component. (It should also be noted that the use of a molar concentration in the estimation of the diffusion constant will lead to a different value of D if the molecular weight value is altered.) Nevertheless, it seems logical that the multiple sequence copolymer, with its styrene segments surrounded by si-

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loxane blocks which are incompatible with the polystyrene matrix, may well adopt a conformation in the melt which is more compact, and hence diffuses more rapidly, than the AB copolymers.

By a comparison of the values of D actually obtained for $S_{75}D_{77}$ and $S_{129}D_{144}$ at 200 °C, it appears that approximately doubling the molecular weight leads to ca. sixfold reduction in D. (The lower limit value for $S_{40}D_{36}$, of course, provides no information on the molecular weight dependence of D; it can only be said not to be inconsistent with the other values.) As Klein and Briscoe[2] have pointed out, previous studies of polymer self-diffusion have led to quite discordant conclusions on the dependence of D on M. Their careful work with polyethylene, however, supports the conclusion that $D \propto M^{-2}$, consistant with the prediction of deGennes' "reptation" model.[5] While the present limited results suggest a slightly higher order dependence in this case, it is perhaps interesting that the difference is not larger. While the styrene segment moving through the homopolymer matrix may well undergo the motion envisioned in deGennes' model, it is not at all clear what the frictional contribution of the incompatible (and hence presumably rather compactly coiled) siloxane block will be.

Acknowledgment. I am indebted to Dr. J. W. Dean, who kindly provided the block copolymer samples, and Mr. G. W. Bender, who assisted with the experimental measurements.

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Correlation between Regio- and Syndiotactic Specificity of Soluble Vanadium-Based Catalysts for Propene Polymerization

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Received April 24, 1979

The syndiotactic polypropylene prepared with a vanadium-based catalyst system contains irregular linkages of propylene units arranged in head-to-head and tail-to-tail sequences. In previous papers,[1,2] the chemical structures of polypropylenes obtained with the catalyst systems, VCl_4 and alkylaluminiums, were studied by ^{13}C NMR. The sequence distribution of inverted propylene units in a polymer chain was found to follow first-order Markov statistics.[1] When propylene unit inversion is a low content, a typical propagation chain was shown to consist of short sequence blocks of "0" units and longer sequence blocks of "1" units,[1,2] as represented by

$$\text{---11111110001111---111100001111---Mt} \qquad (1)$$

Here, a propylene unit is designated by a "0" when propene adds into an active metal–carbon bond by primary insertion, $-CH(CH_3)CH_2Mt$, or by a "1" when propene adds by secondary insertion, $-CH_2CH(CH_3)Mt$, and Mt indicates the metal (vanadium) atom in the catalyst site bound to a growing polymer chain. In view of the above results, we concluded that the propene orientation in the insertion is essentially attributed to the steric effects of the last propylene unit of a growing chain end.

Conversely, on the basis of ^{13}C NMR analysis on ethylene–propylene copolymers, Zambelli et al.[3-5] suggested that the syndiotactic propagation of propene occurs mainly by secondary propene insertion and is controlled by the asymmetry in the last propylene unit of a growing chain end.

In the present study, the correlation between regio- and syndiotactic specificity of the soluble vanadium-based catalyst systems for propene polymerization has been examined. The catalyst systems used in this experiment are given in Table I, together with the stereoregularities in triad fractions and molecular weights of the polypropylene samples obtained at −78 °C. The molecular weight distribution curves of polypropylene samples obtained with these soluble vanadium-based catalysts were unimodal,[6,7] and the polydispersities ($\bar{M}_w/\bar{M}_n$) were lower than 2.0, indicating that the polymerization of propene with the respective catalyst proceeds on uniform (homogeneous) catalyst sites. The stereochemical triad compositions were determined from the triad peaks of primary carbon resonance ($P_{\beta\beta}$)[8] in the ^{13}C NMR spectra of polypropylene samples. Table II shows the mole fractions of different dyads and triads of connecting propylene units in each sample. The dyad and triad fractions of propylene units, 0 and 1, were determined from the secondary and tertiary carbon resonance peak areas, respectively, in the ^{13}C NMR spectra by the same method used in our previous paper.[1] In the table, F_{00}, F_{11}, F_{01}, F_{10}, F_{000}, F_{111}, F_{001}, F_{011}, F_{100}, F_{110}, F_{101}, and F_{010} represent the mole fractions of 00, 11, 01, 10, 000, 111, 001, 011, 100, 110, 101, and 010 propylene unit sequences in a sample, respectively. Table II indicates that the regioselectivity of propene inserting into an active metal–carbon bond is mainly affected by the kind of alkylaluminium component and decreases as

$$AlEtCl_2 \simeq Al_2Et_3Cl_3 \simeq AlEt_2Cl > AlEt_2Br \geq AlEt_3 \qquad (2)$$

The relation between the syndiotactic triad fraction, $[rr]$, and the heterotactic dyad fraction of connecting propylene units, $[F_{01} + F_{10}]$, is shown in Figure 1. The syndiotactic triad fraction, $[rr]$, decreases with an increase in the amount of $[F_{01} + F_{10}]$. A good correlation between the regioselectivity of an inserting propene and the syndiotactic propylene unit composition seems to support the hypotheses that both the regio- and the syndiotactic spe-

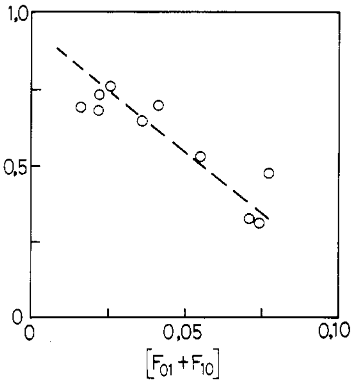

Figure 1. Relation between the syndiotactic triad fraction, $[rr]$, and the heterotactic dyad fraction of connecting propylene units, $[R_{01} + F_{10}]$, in polypropylenes obtained at −78 °C with various soluble vanadium-based catalyst systems.