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Notes

On the Surface Morphology of Block Copolymers

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Block copolymers composed of segments having different surface energies are useful additives for the surface modification of bulk polymers.[1,2] The surfaces of samples of the block polymers themselves, as well as mixtures containing them, are substantially enriched in the component of lower surface energy.[1–3] Recently, X-ray photoelectron spectroscopy has provided direct confirmation of such surface enrichment.[4–6] These studies have demonstrated, however, that quite different surface morphologies may exist. With dimethylsiloxane-containing copolymers, a substantially complete siloxane surface layer is found, confirming the earlier inference from wettability and surface tension measurement.[1,2,7] Ethylene oxide–styrene block copolymers, on the other hand, have surfaces composed of separate styrene and ethylene oxide domains, although the former are in higher concentration and seem to protrude.[6]

The thermodynamic criterion for liquid spreading provides a rationale for these observations. In order for liquid b to spread over the surface of liquid a, it is necessary that the spreading coefficient,[8] $S_{b/a} = \gamma_b - (\gamma_a + \gamma_{ab})$ (the γ's being the surface tensions and γ_{ab} the interfacial tension between the liquids), be positive. If $|\gamma_a - \gamma_b| < \gamma_{ab}$, neither liquid can spread on the other. If this condition applies at the block copolymer surface during its formation, the isolated domain morphology is to be expected.

The low surface tension of poly(dimethylsiloxanes) (PDMS), relative to other polymers, favors spreading. Available data[9] indicate that in all cases where all three tensions have been measured, PDMS will spread. With few exceptions, the surface tension of PDMS is at least 10 dyn/cm lower than that of other polymers, while very few polymer interfacial tensions measured to date exceed this magnitude. The most likely candidates for the existence of the nonspreading condition with PDMS are the fluorinated polymers (the only polymers whose surface tensions are close to that of PDMS; a substantial interfacial tension between perfluoroalkanes and PDMS also exists[10]), and possibly poly(butylene oxide), for which $(\gamma_a - \gamma_b) =$ 4.7 dyn/cm at 150 °C.

Similarly, in the case of ethylene oxide–propylene oxide (PEO–PPO) block copolymers, for which surface tension measurements imply a substantially complete PPO surface,[3] the difference in surface tension of the homopolymers is $\sim$12 dyn/cm, while measured interfacial tensions range from 1.3 to 2.8 dyn/cm;[11] thus PPO is expected to spread over PEO.

For styrene–ethylene oxide copolymers (PS–PEO), on the other hand, the homopolymer surface tensions differ by only $\sim$2 dyn/cm. No direct measurement of interfacial tension between PEO and PS has apparently been reported; however, I have measured[12] γ_{ab} between ethylene glycol and ethylbenzene as 10.6 dyn/cm at 23 °C. Clearly, this large interfacial tension between the monomer analogues is entirely consistent with the nonspreading behavior implied by the observed isolated domain morphology.[13]

When values of all three tensions are available, the surface morphology may be predicted. Thus, literature data[9] yield a value of $S^{150\ °\mathrm{C}} = +5.9$ dyn/cm for the spreading of poly(*n*-butyl methacrylate) on poly(methyl methacrylate), suggesting that a block copolymer would exhibit a substantially complete poly(butyl methacrylate) surface layer. On the other hand, $S^{150\ °\mathrm{C}} = -4.6$ dyn/cm for poly(isobutylene)–poly(vinyl acetate), leading to the expectation of an isolated domain morphology for such a block copolymer.

Of course, surface and interfacial tensions vary with both temperature and molecular weight, and it is not obvious how much such variations will alter the values which are relevant to the actual process of surface formation for a particular block copolymer sample. It would also appear that geometrical limitations (e.g., for a short block of the surface-active component, especially in a repeating block or ABA copolymer where it is constrained at both ends by attached matrix blocks) might preclude effective spreading. In the cases cited above, the relatively large magnitude of the spreading coefficients (positive or negative) lend confidence to their predictive value. Further study is clearly needed for cases where the relative surface and interfacial tensions are more closely matched.

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(13) The nonspreading of poly(ethylene glycols) on polystyrene has also been confirmed directly; contact angles on a smooth polystyrene surface for the same series of low molecular weight glycols used in our previous work range from 38–47° at 23 °C.

Radiation-Induced Oligomerization of α-Methylstyrene

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It has been established that the radiation-induced polymerization of α-methylstyrene which occurs only when

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the monomer is rigorously dried proceeds by a cationic mechanism.[1] The molecular weight of the polymer produced decreases with increasing temperature,[2] and oligomers are expected to be produced at high temperature. The present study deals with the radiation-induced oligomerization of α-methylstyrene at high temperature, and the results are compared with the catalytic oligomerization of styrene derivatives which has recently been studied by Higashimura et al.[3]

Two types of chain transfer to monomer have been suggested to occur on the basis of the infrared spectrum of the polymer produced by the irradiation of α-methylstyrene.[4] One is the direct β-proton transfer from the propagating cation to form an unsaturated end group. Another is the proton transfer following the electrophilic substitution of the penultimate benzene ring by the propagating cation to form a substituted phenylindan end group.[5] The present study gives information about the chain-transfer mechanisms at high temperature.

In our previous study on the radiation-induced degradation of poly(α-methylstyrene) at high temperature it was suggested that a dimer, 1,1,3-trimethyl-3-phenylindan (TMPI), is formed by a cationic chain reaction along the polymer chain.[6] In the present study the oligomerization was studied at temperatures up to 197 °C, and the contribution of degradation of the propagating cation to dimer formation is discussed.

Experimental Section

Commercially obtained α-methylstyrene was purified by the usual method and dried over calcium hydride. Rigorous drying and the preparation of samples were carried out with a high-vacuum line ($\sim 10^{-6}$ mmHg). The monomer was repeatedly dried over barium oxide, which had been baked for 72 h at 400 °C, in a Pyrex flask fitted with a break seal. After the sample tubes were baked overnight, the monomer was introduced into the tubes by trap-to-trap distillations. The samples were irradiated in an electric furnace with ^{60}Co γ rays at a dose rate of 3.5×10^5 rd/h for 1 h. The temperature was maintained constant to within 2 °C. The yield of the dimer, TMPI, was determined by gas chromatography on an Apiezon L column. The molecular weight distribution of oligomers was measured by gel permeation chromatography in tetrahydrofuran after evaporating the remaining monomer under reduced pressure. The measurement was carried out with a differential refractometer and two 2-ft columns packed with TSK-Gel 1000H (nominal porosity, 40 Å) at a 1.5 mL/min flow rate.

Results

The molecular weight distributions of the products at various temperatures up to 197 °C are shown in Figure 1. The peaks at elution counts of 24.3, 22.0, 20.5, and 19.3 correspond to dimer, trimer, tetramer, and pentamer, respectively, and the sharp peak at 16.2 counts includes higher polymers.[7] The figure shows that the molecular weight of the product decreases with increasing temperature. The peak at 16.2 counts becomes negligibly small above 66 °C. This means that low molecular weight oligomers are predominantly produced above the ceiling temperature of the monomer, 61 °C.[8]

A dimer was produced with detectable yields at 41 °C and above, and the yield of the dimer increased with increasing temperature. The dimer was identified as TMPI by its NMR and mass spectra. It has been reported that other dimers, 4-methyl-2,4-diphenyl-1- and -2-pentanes, are produced together with TMPI in the catalytic oligomerization of α-methylstyrene at 50 °C.[3b] However, in the radiation-induced oligomerization these unsaturated dimers were not detected in the temperature range studied. The yields of the dimer, oligomers, and polymer were negligibly small when the monomer was not rigorously dried.

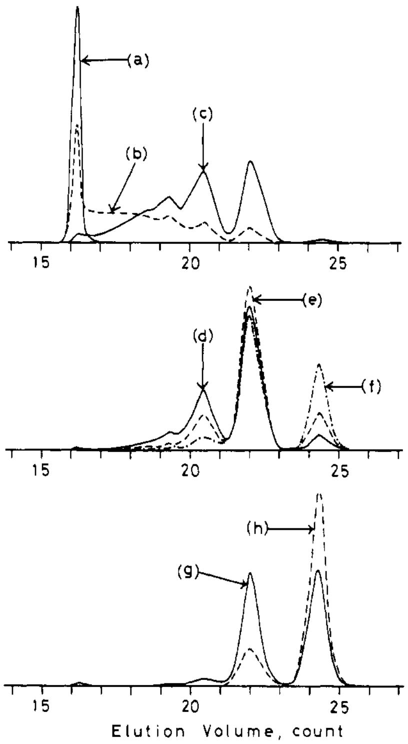


Figure 1. Distribution of oligomers. Temperatures: (a) 30 and 41 °C; (b) 56 °C; (c) 66 °C; (d) 84 °C; (e) 103 °C; (f) 133 °C; (g) 149 °C; (h) 197 °C.

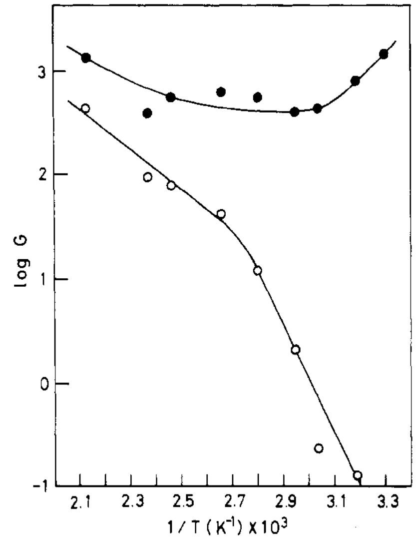


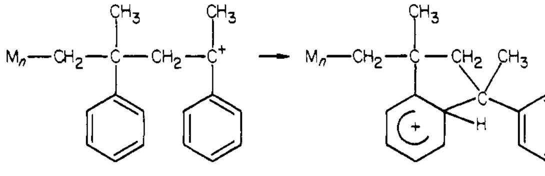
Figure 2. Temperature dependence of the G(TMPI) (○) and G(−m) (●) values.

Temperature dependence of the G value of TMPI, G(TMPI), is shown in Figure 2 together with that of the monomer consumption, G(−m).[9] The yield of TMPI based on the consumed monomer rises to 64% at 197 °C, the highest temperature studied. The Arrhenius plot of G(TMPI) appears to be broken at about 90 °C, and the activation energies at the lower and higher temperature regions are 23 and 9 kcal/mol, respectively. The result suggests that two different mechanisms of dimer formation exist.

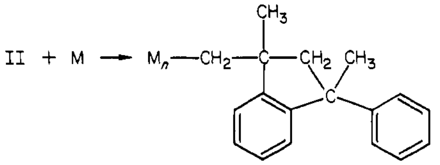
The mixtures of oligomers produced above 56 °C were submitted to NMR spectrometry, and no olefinic proton was detected, indicating that the oligomers have substituted phenylindan end groups.

Discussion

The products having unsaturated end groups were not detected, which indicates that at high temperatures cyclization of the propagating cation (eq 1) occurs in preference to direct β-proton transfer to monomer.



I II (1)

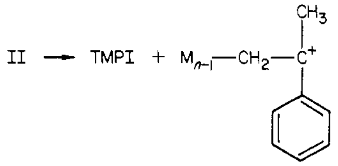


(2)

In eq 1 and 2 M denotes monomer and n, the number of monomer units. Cyclization results in cessation of propagation by cation I, and the decrease in molecular weight with increasing temperature should be due to the increase in the rate of cyclization.

In the oligomerization of styrene derivatives by cationic catalysts it has been concluded that cyclization predominates over β-proton elimination when the cation–anion interaction is weakened on the basis of the effects of counteranions and solvents on the composition of dimers.[3e] The propagating ion of radiation-induced polymerization is known to be a free ion,[1] and the result of the present study indicates that β-proton elimination cannot compete with cyclization in the case of the free cation.

The dimer is produced by reactions 1 and 2 as well as higher oligomers. Another possible process of dimer formation is the elimination of TMPI from cation II, which has been proposed in the radiation-induced degradation of poly(α-methylstyrene) at high temperature.[6]



(3)

The reaction is the protolysis of the C–C bond by the proton derived from the aromatic ring to give the neutral product and the stable tertiary carbonium ion and competes with the proton transfer to monomer (eq 2). The dimer is formed by a chain reaction (reactions 1 and 3) when cation I has a long chain. It is worth noting that oligomers other than the dimer were not produced in the radiation-induced degradation of poly(α-methylstyrene). It seems reasonable to assume that degradation contributes to dimer formation at lower temperatures, where dimer formation has the higher activation energy (Figure 1). In contrast, at higher temperatures the concentration of the propagating cation having a sufficiently long chain to yield the dimer by degradation is limited, and the dimer is predominantly formed by reactions 1 and 2.

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Translational Diffusion and Hydrodynamic Radius of Unperturbed Flexible Chains

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Rapid development of quasi-elastic light scattering technique during the past few years has furnished highly accurate measurements of translational diffusion coefficients, making possible a fairly rigorous test of dynamic theories for flexible macromolecules in solution. In this note we summarize all the existing experimental results for polystyrene in Θ solvents and find significant disagreement with the well-known expressions of Kirkwood[1] or Zimm[2] for the diffusion coefficient. At present no satisfactory explanation is known for this discrepancy, which has been pointed out[3-7] previously on the basis of more limited data.

Following common practice, we may define an average reciprocal hydrodynamic radius in terms of the Stokes law expression

$$\langle 1/R_\mathrm{h}\rangle_z = (6\pi\eta_0/k_\mathrm{B}T)D_z \qquad (1)$$

where η_0 is solvent viscosity, $k_\mathrm{B}T$ the thermal energy, and D_z the measurable z-average translational diffusion coefficient. The hydrodynamic radius may then be compared to the observable root-mean-square z-average radius of gyration $\langle S^2\rangle_z^{1/2}$ in terms of the dimensionless number

$$\rho = \langle S^2\rangle_z^{1/2}\langle 1/R_\mathrm{h}\rangle_z^{1/2} \qquad (2)$$

which is independent of chain length.

For monodisperse polymers, according to the relation of Kirkwood[1,8]

$$D = k_\mathrm{B}T/(\eta_0 P\langle 6S^2\rangle^{1/2}) \qquad (3)$$

with

$$P = (3\pi)^{3/2}/2^{5/2} = 5.115 \qquad \rho = 1.504$$

while the Zimm theory (which preaverages the hydrodynamic interactions) leads to

$$P = (3/2)^{1/2}\pi\Gamma(3/4)/\Gamma(5/4) = 5.202 \qquad \rho = 1.479 \qquad (4)$$

the difference between the two expressions being due to coupling between internal and translational motions (im-

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