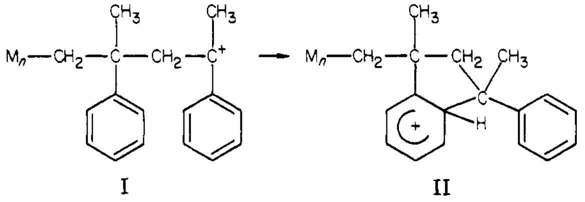
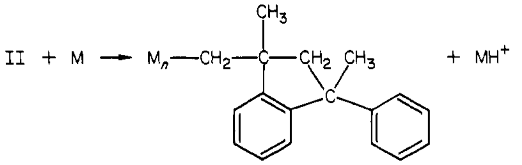
Discussion

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.



(1)

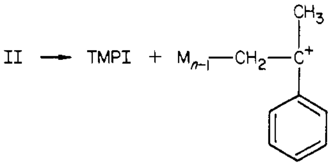


(2)

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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Received September 29, 1980

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

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

where η_0 is solvent viscosity, $k_{\rm B}T$ 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

$$\rho = \langle S^2\rangle_z^{1/2}\langle 1/R_{\rm h}\rangle_z^{1/2} \tag{2}$$

which is independent of chain length.

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

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

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

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

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

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Macromolecules 1981, *14*, 211-212

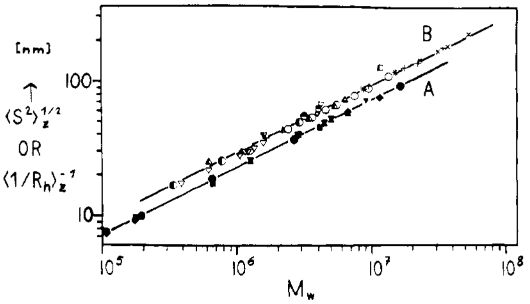

Figure 1. Hydrodynamic radius, $\langle 1/R_h\rangle_z^{-1}$, and radius of gyration, $\langle S^2\rangle_z^{1/2}$, for linear, nearly monodisperse polystyrene in Θ solvents. Data sources: Curve A: (♦) ref 4; (▼) ref 10; (●) ref 11; (▲) ref 3; (■) ref 12. Curve B: (○) ref 15; (⊟) ref 19; (⊖) ref 20; (+) ref 13; (×) ref 17; (◐) ref 16; (◘) ref 4; (▽) ref 18; (△) ref 14; (▼) ref 21; (▲) ref 22.

plicitly not taken fully into account in the Kirkwood formulation) and amounting to only 1.7%. The data, as we now show, differ from the above numbers by a considerably larger amount. Figure 1, curve A, exhibits the diffusion data reported by many different investigators.[3,4,10-12] They are well correlated by the expression

$$\langle 1/R_h\rangle^{-1} = 0.0229 M_w^{1/2} \qquad (\pm 1.7\%) \qquad (\text{nm}) \qquad (5)$$

For radii of gyration[4,13-22] we have limited consideration to measurements since 1970, thus taking proper account of improvements in technique, and find (curve B)[4,13-17] the result

$$\langle S^2\rangle_z^{1/2} = 0.0290 M_w^{1/2} \qquad (\pm 2.5\%) \qquad (\text{nm}) \qquad (6)$$

Thus we obtain

$$\rho(\text{exptl}) = 1.27 \pm 0.06 \qquad (7)$$

which is seen to be about 15% lower than the theoretical values quoted above. Similar results have been obtained recently with PMMA in a Θ solvent, where a value of $\rho = 1.16$ was found.[23]

No rigorous analytical expression has yet been derived for flexible chains with full unpreaveraged hydrodynamic interactions. A very recent Monte Carlo study by Zimm[24] avoids preaveraging and indeed leads to the result $P = 6.0$, $\rho = 1.28$, in close agreement with the experiments. Unfortunately there is reason[25] to question one aspect of Zimm's procedure; and a different approach, via Brownian dynamical simulation, so far suggests[25] that the Kirkwood formula is within 3% of the right answer for the given model. One may thus be forced to conclude that deficiencies in the model itself (e.g., Oseen perturbation formula treating chain elements as point centers of hydrodynamic resistance, assumed additivity of these interactions, possibility of singularities,[26] etc.) may have to be explored further.

Acknowledgment. We are grateful to Professor W. H. Stockmayer for many valuable discussions and suggestions. This work was supported by the Deutsche Forschungsgemeinschaft (W.B. and M.S.). M.S. thanks the Alexander von Humboldt-Stiftung for a Feodor-Lynen-Forschungsstipendium.

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Structure of Noncrystalline Isotactic Poly(methyl methacrylate). Evidence against Double Helices

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Received July 2, 1980

The proposal made in 1976[1] that the molecules of crystallized isotactic poly(methyl methacrylate) (i-PMMA) are double helices was the first indication that a nonbiological polymer molecule could exhibit a double-strand structure. To date it still stands as the only example of such behavior. However, examination of the wide-angle X-ray scattering (WAXS) patterns of i-PMMA in its noncrystalline form (as a glass), using both isotropic and oriented specimens, shows that the molecules in this form are neither paired nor regularly intertwined.

Most of the recent conformational energy calculations for i-PMMA have shown that conformations near to all-trans have the lowest energies.[2-6] Such conformations (based on bond rotation sequences ...ϕ_1, ϕ_2, ϕ_1, ϕ_2... with ϕ_1 and ϕ_2 both near zero) will form sinuous helices (except where $\phi_1 = -\phi_2$ where rings are formed). They are thus unlikely to occur in crystal structures unless paired into double helices.

The crystalline conformation of i-PMMA is, however, still the subject of disagreement. Early suggestions were of a 5/2 helix[7] and a 5/1 helix.[2,8-10] More recently, Tadokoro and co-workers[1] have reinterpreted the fiber pattern of crystalline i-PMMA in terms of double helices, each strand of which is a sinuous 10/1 helix ($\phi_1 = 32°$, $\phi_2 = 1°$) but this conclusion has been contested.[11]

Figure 1 shows the WAXS from quenched, and thus noncrystalline, i-PMMA compared with that from syndiotactic and atactic PMMA (s-PMMA and a-PMMA). It can be seen that there is considerable similarity between the three curves, particularly at high s. The scattering from i-PMMA differs from that from s-PMMA in that the first peak (at $s = 0.95$ Å^{-1} for all three polymers) is symmetrical. WAXS from a- and s-PMMAs oriented by

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