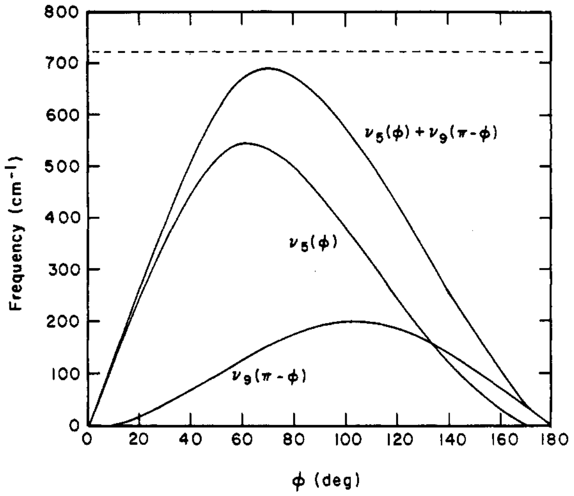

Figure 6. Zone-center frequencies of the binary combinations obtained by adding $\nu_5(\phi)$ and $\nu_9(\pi-\phi)$. The dashed line indicates the frequency near 725 cm^{-1} of the intense methylene rocking mode fundamental, from which the binary combinations borrow intensity. (See text and ref 9 for a fuller explanation.)

twisting modes, respectively. These curves are depicted in Figure 6 for the isolated chain. Interchain interaction in the crystal complicates the picture, but its effect is primarily in the frequency region near the zone center ($\phi = 0$ and π). Thus, the isolated-chain approximation is quite good in the region in which we are interested, since it is well away from the zone center. The ν_5 and ν_9 curves in Figure 6 were computed with a standard valence force field[11] and then scaled somewhat so that their cut-off frequencies have the generally accepted values determined from neutron scattering. These values are 550 cm^{-1} for ν_5 and 200 cm^{-1} for ν_9.[12]

The two possible zone-center combinations are $\nu_5(\phi)+\nu_9(\phi)$ and $\nu_5(\phi)+\nu_9(\pi-\phi)$.[9] The latter combination, shown in Figure 6, has a critical point at 690 cm^{-1}, nearly exactly at the frequency of the band in question.

The symmetry of half the binary combinations $\nu_5(\phi)+\nu_9(\pi-\phi)$ is correct for interaction with the 720-cm^{-1} band. This can be easily shown for a chain having an odd number of carbons. The point group of this chain is C_{2v}. If symmetry species A_1 and B_1 contain the in-plane modes (ν_5) and A_2 and B_2 contain the out-of-plane modes (ν_9), then the binaries $A_1 + B_2$ and $B_1 + A_2$ have the B_2 symmetry of the 720-cm^{-1} fundamental so that interaction will occur. A similar argument can be made for even chains. We note that the interaction between the 720-cm^{-1} fundamental and the binary combinations is actually very weak, just sufficient to make the binary combinations observable.

For PE, effectively an infinitely long chain, the result is a single, broad band at 690 cm^{-1} that consists of a continuum of overlapping components. For the *n*-alkanes, the frequency separation between the binaries is large enough to permit individual bands to appear. The higher frequency components tend to be the more intense because they are closer to and hence can interact more strongly with the 720-cm^{-1} fundamental. The fact that these bands depend on chain length and crystal structure is now understandable, since both these factors are known to influence the frequencies of the component fundamentals.

Summary

In a recent publication, an infrared band in the spectrum of solid polyethylene was associated with the presence of molecular twist boundaries.[1] Actually, two different bands are involved. One of these appears at 690 cm^{-1} in the spectra of bulk- and solution-crystallized polyethylene; the other, which is much more intense, is reported to appear at 680 cm^{-1} in the spectrum of a partially annealed polyethylene glass obtained by rapid quenching of the melt.[4] In their paper on twist boundaries, the authors refer to both bands as the "680 cm^{-1} band".

We are concerned here with the assignment of the 690-cm^{-1} band. Bands similar in frequency and intensity are observed in the spectra of long crystalline *n*-alkanes, which are known to be comprised of planar chains. An analysis of these bands indicates that the 690-cm^{-1} band is to be assigned to a Fermi-resonance-enhanced series of binary combinations. The assignment accounts well for the main features of the 690-cm^{-1} band.

Acknowledgment. We gratefully acknolwedge support by the National Science Foundation (Grant No. DMR-84-03711). H.H thanks the Swiss National Science Foundation for a postdoctoral fellowship. We thank Professor Herbert Strauss for helpful comments.

Registry No. $C_{18}H_{38}$, 593-45-3; $C_{20}H_{42}$, 112-95-8; $C_{21}H_{44}$, 629-94-7; $C_{22}H_{46}$, 629-97-0; $C_{23}H_{48}$, 638-67-5; $C_{24}H_{50}$, 646-31-1; $C_{25}H_{52}$, 629-99-2; $C_{26}H_{54}$, 630-01-3; $C_{27}H_{56}$, 593-49-7; $C_{28}H_{58}$, 630-02-4; $C_{29}H_{60}$, 630-03-5; $C_{30}H_{62}$, 638-68-6; $C_{36}H_{74}$, 630-06-8; polyethylene, 9002-88-4.

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(13) These spectra were measured with the use of an IR-7 Beckman infrared spectrometer with a resolution of better than 2 cm^{-1}. The *n*-alkanes were measured in KBr pellets. Several of the *n*-alkanes were also measured as films with the Nicolet FTIR spectrometer. The spectra are the same in both cases except near 667 cm^{-1}, where the Beckman spectra show anomalies due to the intense CO_2 band at this frequency.

Reduction of the Unperturbed Dimensions of the Main Chain When Ethyl Groups Are Attached to a Poly(methylene) Backbone

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Branched and linear polymers with the same number of bonds, N, have different mean square radii of gyration, $\langle s^2 \rangle$.[1] The ratio of the two $\langle s^2 \rangle$ is commonly denoted by g. The value of g in the unperturbed state can be calculated by random flight statistics,[1] rotational isomeric state theory,[2,3] or the wormlike-chain model.[4] Rotational isomeric state theory most easily takes into account the influence of a branch on the probability for occupancy of individual rotational isomers accessible to bonds near a

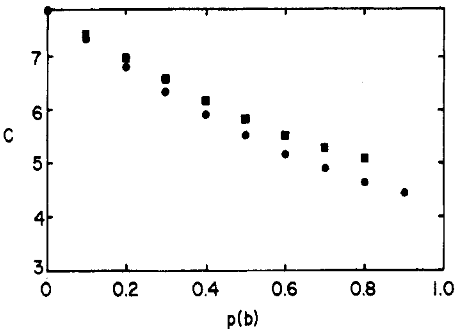

Figure 1. Characteristic ratio, C, of the main chain as a function of the fraction of the monomers that are 1-butene, $p(\mathrm{b})$, for $\tau = 0$ (circles) and 0.43 (squares).

branch point.[5] Of course, the influence on $\langle s^2 \rangle$ of this alteration in the population of rotational isomers becomes smaller as the number of bonds increases while the number of branches remains constant. For this reason, rotational isomeric state theory and random flight statistics predict identical values of g for starlike branched molecules in the limit where N becomes infinite, although they may yield different values of g when N is small.[3] The common limit at large N is obtained because the mean square end-to-end distance, $\langle r^2 \rangle$, is unaffected by the presence of a *single* branch if a chain contains a sufficiently large number of bonds.

Now consider a "linear low-density polyethylene" in which an increase in N is accompanied by an increase in the number of short branches. An example is provided by copolymers of 1-butene and ethylene that differ in molecular weight but not in monomer ratio. The influence on the main chain of the disturbance in rotational isomers near a branch point is not diluted as the molecular weight increases. Short branches therefore retain an influence on $\langle r^2 \rangle$ at all degrees of polymerization. In the high molecular weight limit, $\langle s^2 \rangle = \langle r^2 \rangle / 6$ if the short branches are randomly distributed. Hence *short* branches cause $\langle s^2 \rangle$ for the copolymer to be different from $\langle s^2 \rangle$ for a linear chain that has the same number of bonds as the main chain. The direction and magnitude of the effect are evaluated here for random copolymers of 1-butene and ethylene.

Calculations

The characteristic ratio, C, is defined as the ratio of the mean square unperturbed end-to-end distance, $\langle r^2 \rangle_0$, to the sum of the squares of the lengths of the n bonds in the main chain. The value of $\langle r^2 \rangle_0$ was calculatd by rotational isomeric state theory[6] in a form that incorporates the influence of articulated side chains on the configurational statistics of the main chain.[5,7] Ethyl branches are distributed in the manner expected for random copolymers of ethylene and 1-butene when the monomers have equal reactivity. The sequence of the monomer units in a particular chain is determined by $(n + 1)/2$ random numbers and the probability, $p(\mathrm{b})$, that a monomer unit is 1-butene. There is no preference for attachment of ethyl groups to the backbone in either the *d* or *l* configuration. Values of C reported for a particular $p(\mathrm{b})$ are averages over 1000 chains of different monomer sequence and stereochemistry.

Values of most of the parameters are taken from the well-known rotational isomeric state model for unperturbed poly(methylene).[8] The bond angle is 112°. Gauche states are located at ±120° from the trans state. First- and second-order interactions are weighted by using $\sigma = 0.43$ and $\omega = 0.034$, which are values appropriate for a temperature of 300 K. An additional statistical weight, denoted by τ, is required at each bond to an atom that

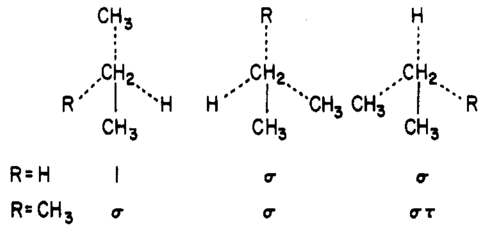

Figure 2. Three rotational isomers of CH_3–CH_2–CHR–CH_3 viewed along the internal C–C bond. The two sets of statistical weights are those expected when R = H $(1, \sigma, \sigma)$ and when R is equivalent to a methyl group $(\sigma, \sigma, \sigma\tau)$.

constitutes a trifunctional branch point.[9] Calculations were performed with $\tau = 0$ and $\tau = \sigma$. There are 1000 bonds in the main chain.

Results and Discussion

Figure 1 depicts the change in C with increasing $p(\mathrm{b})$ in random copolymers of ethylene and 1-butene. Random incorporation of 1-butene produces a monotonic decline in C that is slightly more precipitous at lower $p(\mathrm{b})$. The larger value of τ yields higher C, but there is only a small sensitivity of C to plausible variation in τ. The copolymer with $p(\mathrm{b}) = 0.5$ has a main chain with a C that is only about 70% as large as that seen with linear polyethylene. A depression in C of 10% occurs when there is an ethyl group bonded to one out of every 12–14 main-chain carbons.

The negative sign for $\mathrm{d}C/\mathrm{d}p(\mathrm{b})$ is easily rationalized with the aid of Figure 2. This figure depicts the three rotational isomers for CH_3–CH_2–CHR–CH_3. The view is along the internal C–C bond. The statistical weights are 1, σ, and σ when R = H, and the probability for a trans placement is $1/(1 + 2\sigma)$. The statistical weights change to σ, σ, and $\sigma\tau$ when R is equivalent to a methyl group. Now the probability for a trans placement of the two CH_3 groups is $1/(2 + \tau)$. The molecule with R = H has the higher probability for a trans placement of the two CH_3 groups if $2\sigma < 1 + \tau$. This inequality is satisifed for realistic σ and τ.

The foregoing analysis, which neglects the influence of second-order interactions, implies there will be a decrease in the probability for a trans placement, $p(\mathrm{t})$, at bonds in the main chain when R behaves as a methylene group insofar as first-order interactions are concerned. This expectation is supported by more rigorous calculations that employ the complete matrix expression for the configuration partition function.[10] The results extracted from the configuration partition function show a monotonic decrease in $p(\mathrm{t})$ from 0.64 in the absence of 1-butene to 0.52 ± 0.02 as $p(\mathrm{b})$ approaches 1. The negative sign for $\mathrm{d}C/\mathrm{d}p(\mathrm{b})$ is a natural consequence of the decrease in the probability for a trans placements in the main chain.

Acknowledgment. These calculations were performed at the suggestion of Leo Mandelkern, who suspected that the dimensions of the main chain would be sensitive to the branch content. The research was supported by National Science Foundation Grant DMR 83-15547.

Registry No. (1-Butene)·(ethylene) (copolymer), 25087-34-7.

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Diffusion Measurements of Poly(methyl methacrylate) in Semidilute Solutions of Polystyrene in Thiophenol with an Analytical Ultracentrifuge. Dynamics of Polymer–Polymer–Solvent Ternary Systems. 3

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In a previous paper,[1] referred to as part 2 hereafter, we studied the diffusion and the sedimentation behavior of poly(methyl methacrylate) (PMMA) in mixtures of polystyrene (PS) and thiophenol (TPh) over wide ranges of both concentration and molecular weight of PS by using the dynamic light scattering (DLS) and the sedimentation velocity (SV) techniques. In the study, we compared the reduced quantity D/D_0 with the corresponding reduced quantity s/s_0. Here D_0 and s_0 are values of D and s in pure thiophenol extrapolated to infinite dilution. The two reduced quantities should be identical if the same friction coefficient f were effective for both diffusion and sedimentation even in the semidilute regime where polymer dynamics are greatly affected by the intermolecular interaction between polymer chains. It was found that (1) as far as molecular weight of PS, M_{PS}, was lower than that of PMMA, M_{PMMA}, the ratios were in good agreement with each other within experimental uncertainties; (2) when M_{PS} was higher than M_{PMMA}, D/D_0 was smaller than s/s_0 by more than 30% at higher c_{PS}. Taking into account that time and spatial scales of DLS (ms and μm) and SV measurements (min and mm) are different for more than 3 orders of magnitude, we attributed the observed difference between D/D_0 and s/s_0 to the cause that the frictional force experienced by a PMMA molecule in the PS solutions depended on the relaxation time characteristic of the surrounding medium.[2,3] In order to examine this conjecture, we have attempted one classical diffusion measurement on the same solutions, of which time and spatial scales are comparable with those of SV measurements. Only preliminary results were reported in part 2. Here we report results of a more systematic study.

Polymer samples of PMMA and PS used are the same as those used in part 2; M_{PMMA} = 343 000, and M_{PS} = 43 900, 775 000 and 8 420 000, respectively. Polymer solutions were prepared by exactly the same way as described in part 2. The concentrations of polymer in solutions were determined by weighing.

Diffusion experiments were performed at 25 ± 0.05 °C by making use of an analytical ultracentrifuge (Beckmann Spinco Model E). Since the principle of the technique is described in detail in texts,[4] experimental procedures are here mentioned only briefly. The synthetic boundary method, which uses a cell with double sectors connected with a capillary, has been adopted. One sector is filled with a solution of PS in TPh as a solvent and the other is half-filled with a ternary solution of PMMA and PS in TPh with exactly the same c_{PS} as that of the solvent. Under a small centrifugal force, the solvent in the former sector flows into the latter sector through the capillary and a sharp synthetic boundary is formed. The spreading of the synthetic boundary with time due to the diffusion of PMMA has been detected by using the schlieren optics. D has been estimated from eq 1, where A and H are an

$$(A/H)^2 = 4\pi Dt(1 - z) \quad (1)$$

area and a peak height of the schlieren pattern at time t, and z is a factor that corrects the sharpening effect of the pattern due to the concentration dependence of s.

$$z = 2r_0\omega^2 k_S c_0 s(0)(H/A)t \quad (2)$$

Here r_0 is a distance from the center of rotation to the meniscus, k_s is the concentration coefficient of s, ω is the angular frequency of rotation, and $s(0)$ is the value of s at infinite dilution of PMMA. Since eq 1 holds only for $z \leq 0.16$, ω was made as low as possible to keep z smaller than 0.08.

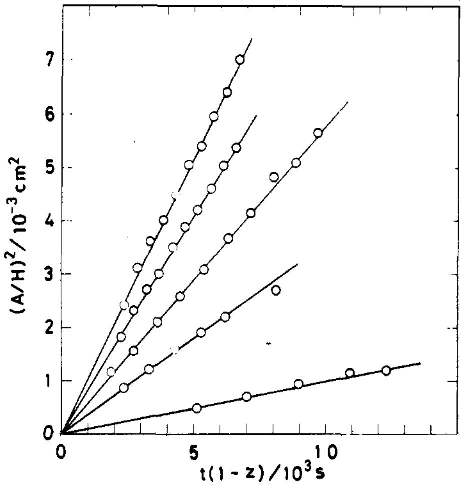

Figure 1. Data analysis for the diffusion behavior of PMMA in solutions of PS (M_{PS} = 43 900, F4 series) with eq 1. From the top, c_{PS} = 1.01, 3.01, 5.00, 9.99, and 16.8%.

The reliability of the method has been tested by comparing D data of dilute PMMA solutions in TPh with those obtained by DLS.[5] By fitting the data to eq 3,

$$D = D_0(1 + k_D c_{PMMA}) \quad (3)$$

we obtained $D_0 = 1.30 \times 10^{-7}$ cm^2 s^{-1} and $k_D = 46$ cm^3 g^{-1}. By comparing these values with $D_0 = 1.32 \times 10^{-7}$ cm^2 s^{-1} and $k_D = 63.8$ cm^3 g^{-1} obtained from DLS measurements, we may say that agreement is excellent for D_0 but less satisfactory for k_D. Thus the macroscopic method we adopted for diffusion measurements tends to give a D value smaller than true one at finite c_{PMMA}. The difference is however only 5% at the highest concentration of c_{PMMA} = 0.2% measured and is about 2% at c_{PMMA} = 0.1%, at which most D data were obtained. According to Kawahara, an experimental accuracy of the method is at best 5%. Therefore the differences at finite c_{PMMA} still remain within an experimental error of 5%. This indicates that D can be accurately determined with this classical method as long as experiments are carefully performed.

Figure 1 illustrates data analysis with eq 1 on PMMA in a series of solutions of PS with M_{PS} = 43 900 from the dilute to the semidilute regime. The plots are well represented by solid straight lines and the slope provides an estimate of D to an accuracy of about 10%.[6] D thus obtained has been reduced to $(D/D_0)_{AU}$ by using the value of D in pure thiophenol, $D_0 = 1.30 \times 10^{-7}$. In Figure 2 the present data of $(D/D_0)_{AU}$ are compared with earlier data

0024-9297/86/2219-2305$01.50/0