Erb[31] and Hilliard[32] for these deficiencies is that regular solution theory on which the Cahn–Hilliard model is based may not fully describe the behavior of either small molecule or polymer systems.

The question of why this high molecular weight system should phase-separate on a much smaller scale than the high molecular weight mixtures of PS/PVME remains unanswered. Until we have investigated other systems showing similar behavior (as yet, no other is known), it is not possible to eliminate an explanation in terms of some unique properties of this blend. However, we can at this stage rule out a hypothesis based on "blockiness" in the SCPE.[24] We are continuing this study using monodisperse fractions of both polymers in order to determine the effects of molecular weight on the initial phase size and hence to test the entanglement theory of Pincus.

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Registry No. PMMA (homopolymer), 9011-14-7; deuterated PMMA (homopolymer), 98821-48-8.

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Molecular Characterization of Poly(2-methyl-1,3-pentadiene) and Its Hydrogenated Derivative, Atactic Polypropylene

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ABSTRACT: The anionic polymerization of (*E*)-2-methyl-1,3-pentadiene leads to near-monodisperse poly(1,3-dimethyl-1-butenylene) (PDMB). The hydrogenation of PDMB yields atactic polypropylene (PP). We report the complete characterization of the microstructure and thermal properties of these two polymers. The carbon-13 NMR spectral analysis reveals that PP is a head-to-tail, ideal-Bernoullian ($P_m = 0.502$) material. The characteristic ratios for the two polymers were determined under Θ conditions, and, for the case of PP, good agreement is found with the value calculated by Suter and Flory using the five-state rotational isomeric state (RIS) model. The glass transition temperature for the ideal-Bernoullian PP was found to be −2.5 °C, which is about 10 °C higher than values previously reported for non-Bernoullian atactic PP. The conversion of PDMB to atactic PP results in an increase in flexible bonds from three to four along the backbone and in a 28% increase (0.100–0.128 cal g^{-1} °C^{-1}) in the change of heat capacity at T_g between the glassy and liquid states of the respective polymers. Comparisons with previous studies on the thermal properties of PP are discussed.

Introduction

The anionic polymerization of (*E*)-2-methyl-1,3-pentadiene initiated by *n*-butyllithium in benzene solution was first quantitatively examined by Cuzin, Chauvin, and Lefebvre.[2] Their microstructure analysis of poly(2-methyl-1,3-pentadiene), IUPAC name poly(1,3-dimethyl-1-butenylene) (PDMB), demonstrated that the reaction exclusively yields the 1,4-configuration where the cis:trans ratio was approximately 60:40. Later studies by Morton and Falvo[3] showed that monomer incorporation takes place exclusively via 4,1-addition, i.e., where the methyl groups are on the β and δ carbons of the terminal unit. The active center was defined as essentially covalent, an assessment in agreement with current understanding[4] regarding alkyl and primary allylic carbon–lithium bonds in nonpolar solvents. The microstructure analysis of Morton and

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Falvo[3] fortified the finding of Cuzin, Chauvin, and Lefebvre[2] that 1,2- and 3,4-units are not found in these polymers.

PDMB is elastomeric at room temperature. To date, no information exists for PDMB regarding its dilute solution and thermal properties. Thus, in order to obtain data on these topics and to further characterize the microstructure and thermodynamic properties, we have prepared a PDMB series having near-monodisperse molecular weight distribution differing only in sample molecular weight.

Of further interest is the fact that when PDMB is hydrogenated, it is transformed into polypropylene, IUPAC name poly(methylethylene) (PME), with an essentially perfect, in the Bernoullian sense, atactic structure. The first reported[5] method for the preparation of such an atactic material was the epimerization of isotactic PME at 270 °C for extended periods of time. However, the yield was small and the resulting polymer had a broad molecular weight distribution. Recently, Herwig and Kaminsky reported[6] the synthesis of atactic[7] polymer from propylene monomer using a Ziegler–Natta type catalyst consisting of a zirconium compound complexed with aluminoxane. Detailed characterization of the resultant polymers is not yet available.

In the discussion that follows, we describe the synthesis of PDMB and atactic PME and the characterization by NMR, dilute solution measurements, and differential scanning calorimetry of these dissimilar, but related, polymers. The viscoelastic properties of PDMB and PME will be presented in a future paper.

Experimental Section

The purification and polymerization of (*E*)-2-methyl-1,3-pentadiene (Wiley Chemicals Co.) followed the usual general vacuum-line procedures. The purification of the monomer was carried out with the explicit aim of eliminating not only the usual impurities but also, for example, any isomers of (*E*)-2-methyl-1,3-pentadiene that might be present. This procedure is outlined as follows: (a) overnight exposure to calcium hydride with stirring; (b) exposure, with stirring, to sodium dispersion for at least 24 h at room temperature (during this period, a small amount of oligomeric material formed); (c) overnight contact with *n*-butyllithium at room temperature (the slow propagation reaction allows this relatively long-term exposure); (d) storage of monomer over dibutylmagnesium[8] until collected in ampules. Failure to follow this procedure led to polymerizations that yielded moderatley polydisperse material, i.e., M_z/M_w and M_w/M_n ratios of 1.2–1.4. However, GC analysis of the monomer purified in the above fashion did not show the presence of components other than (*E*)-2-methyl-1,3-pentadiene and a small amount of what appeared to be butane. The latter species will be formed from the reaction of either of the foregoing organometallics with proton-bearing impurities. It should also be noted that the sodium and butyllithium "treatments" would be expected to eliminate any foreign dienes since the rate of polymerization of (*E*)-2-methyl-1,3-pentadiene is appreciably less than that of these other species.

Polymerizations were carried out with purified (by distillation) *sec*-butyllithium in benzene at 40 °C. Monomer concentrations ranged from 10 to 40% (v/v). Polymerization times of 5 days to 2 weeks were used. Virtually 100% conversions were obtained in all cases. The molecular weights ranged from 4×10^4 to ca. 3.5×10^5 while the molecular weight distributions were classifiable as near monodisperse.

The molecular weights of the PDMB samples were determined by osmometry and light scattering. The former measurements utilized a Hewlett-Packard 503 osmometer with toluene as the solvent at 37 °C. The weight-average values were determined with a Chromatix KMX-6 low-angle laser light scattering photometer (633 nm). Cyclohexane and tetrahydrofuran were the solvents of measurement. The refractive index increments for PDMB and PME were measured with the Chromatix KMX-16 refractometer. These results are given in Table I.

Table I
Refractive Index Increments for Poly(1,3-dimethyl-1-butenylene) and Poly(methylethylene) at 633 nm

sample	solvent	d*n*/d*c*,[a] mL g^{-1}
PDMB	cyclohexane	0.0989
PME	cyclohexane	0.0588
PME	THF	0.0789

[a] Measurement temperature was 30 °C.

Waters 150C and Ana-Prep instruments having μ-Styragel and Styragel columns, respectively, were used for the size exclusion chromatography (SEC) measurements. Tetrahydrofuran was the carrier solvent at a flow rate of 1 mL min^{-1}. The Θ solvent determinations and the remaining dilute solution characterizations were done with procedures and equipment described elsewhere.[9-11] The Θ solvent of choice was 2-octanol because of the convenient Θ temperature found for PDMB (28.9 °C) and PME (37.6 °C). An additional Θ solvent found for PDMB, to wit, *p*-dioxane at 61.2 °C, was not used for the dilute solution measurements in view of its relatively inconvenient Θ temperature.

The 50.31-MHz ^{13}C NMR measurements were carried out on a Varian XL-200 spectrometer. The PDMB and PME samples were observed at concentrations of 20–25% (w/v). PDMB was dissolved in $CDCl_3$ and studied at 22 °C while the PME materials were placed in a 4:1 mixture of 1,2,4-trichlorobenzene–*p*-dioxane-d_6 and examined at 100 °C. Hexamethyldisiloxane (HMDS) was used as the internal reference in all samples. Spectra were recorded with a 8000-Hz window, a 90° sampling pulse, and repetition times of 3–10 s. Proton-coupled and -decoupled spectra representing 5000–9000 scans were recorded for each sample.

The hydrogenation of the PDMB samples was done with $Pd/CaCO_3$ catalyst (Strem). This catalyst system has been shown previously to lead to the essentially complete hydrogenation of various polydienes.[9-12] As before,[9-12] polymer solutions of ca. 1 g/dL were prepared in cyclohexane. The hydrogenation event was then done under the conditions given by Rachapudy and co-workers.[12] Schulz and Worsfold[13] have reported that the isolation of anionically prepared poly(1-methyl-1-butenylene) followed by resolubilization in cyclohexane leads to incomplete hydrogenation. Suffice it to note that we have not encountered this problem for the case where sufficient catalyst levels were used.[9-11] Schulz and Worsfold[13] chose to use a catalyst level significantly lower than that reported by Rachapudy and co-workers.[12]

All thermal measurements were carried out in a Perkin-Elmer DSC-2C where the temperature scale was set with the melting points of *n*-octane, *m*-, *o*-, and *p*-xylene, water, benzene, and indium at a heating rate of 10 °C min^{-1}. The effect of heating at rates of 0.31, 0.62, 1.25, 2.5, 5, 10, 20, and 40 °C min^{-1} was noted. All of the glass transition measurements were made with a Freon refrigeration system and nitrogen gas purge (25 cm^3 min^{-1}) whereas the specific heat experiments were made with a liquid nitrogen cryostat and helium as the purge (20 cm^3 min^{-1}). The polymer samples were encapsulated in standard aluminum pans and quenched, in the DSC cell, at 40 °C min^{-1} to 50 °C, below the respective glass transition temperature. The subsequent glass transition measurements were done by commencing the heating cycle with the polymer sample at the aforementioned temperature.

Heat capacity measurements were made over the temperature range −50 to +50 °C by comparing the energy input to the calorimeter plus empty sample pan to that of the calorimeter plus pan and sample. Calibration was accomplished with an indium standard using a value of 6.80 cal/g for the heat of fusion. Subsequent measurements of a sapphire sample showed that the measured heat capacity in this temperature range agreed with the known values to within 1%.

Results and Discussion

NMR Measurements. The ^{13}C NMR spectrum of PDMB-H (Table II) is shown in Figure 1. The assignment of the carbon resonances is based on the comparison of coupled and decoupled spectra and on necessary integral ratios. As an example: C_4-c (cis) plus C_4-t (trans) must

Table II
Molecular Characteristics of Poly(1,3-dimethyl-1-butenylene)

PDMB sample	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$[\eta]^{30\ °C}_{THF}$, dL g^{-1}	$[\eta]^{28.9\ °C}_{2\text{-octanol}}$, dL g^{-1}	M_z/M_w[a]	M_w/M_n[a]	M_w/M_n[b]	k_H[c]
B	4.15	4.45	0.47_2	0.23_0	1.04	1.07	1.07	0.77
C	5.02	5.44	0.55_3	0.24_9	1.07	1.08	1.08	0.80
D	5.50	5.87	0.59_0	0.26_9	1.03	1.05	1.07	0.83
E	7.09	7.63	0.71_8	0.30_2	1.03	1.07	1.08	0.88
F	11.7	12.5	1.00_2	0.38_5	1.05	1.07	1.09	0.94
G	16.6	19.0	1.26_8	0.46_5	1.09	1.13	1.14	0.94
H	34.6[d]	37.7	2.18_7	0.65_1	1.09	1.14		1.02

[a] Via Waters 150C and Ana-Prep size exclusion chromatographs. [b] Via light scattering and osometry. [c] θ conditions. [d] From size exclusion chromatography using the calibrations shown in Figure 4.

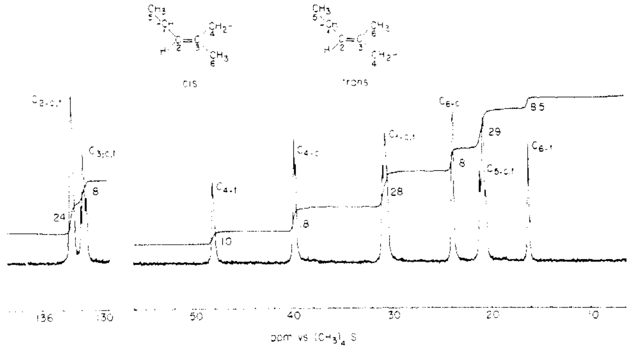

Figure 1. 50.31-MHz ^{13}C NMR spectrum of PDMB-H in CDCl$_3$.

equal C$_1$-c,t (cis and trans). The C$_6$-t resonance is expected to be upfield of C$_6$-c by ~8 ppm because of the eclipsing of C$_6$-*t* by C$_1$. Similarly, C$_4$-c is found upfield of C$_4$-t by ~8 ppm due to the eclipsing of C$_4$-c by C$_1$. These cis and trans shifts are similar to those reported by Duch and Grant[14] for poly(1-methyl-1-butenylene) and poly(1-butenylene). The smaller than expected C$_3$ integral is the result of a very long ^{13}C spin–lattice relaxation (T_1) and possibly less than full nuclear Overhauser enhancement (NOE) for this nonprotonated carbon.

From the integral measurement of the alkyl region, we find a cis:trans ratio of 64:36. This ratio is in good agreement with the results of Cuzin, Chauvin, and Lefebvre[2] (vide supra). Our ^{13}C NMR data show no indication of 1,2- or 3,4-addition during polymerization. The results indicate that the 1,4-content of PDMB is at least 99.4%.

The ^{13}C NMR spectrum of the hydrogenated polymer, PME, is shown in Figure 2 with the methyl, methine, and methylene regions expanded. The polymer is in essence a stereoirregular PME. The many different resonances in each spectral region reflect the sensitivity of the carbon nuclei to the different stereosequences. The details of these assignments, including methyl assignments to the heptad level, have been published by Schilling and Tonelli.[15] A quantitative analysis of the integrals of the methyl triads and pentads (Figure 2a) indicates that the chain statistics resulting from the hydrogenation are Bernoullian with P_m of 0.502. This observation is in contrast to typical stereoirregular PME, which cannot be described by a simple statistical model of polymerization.[15] Thus the hydrogenation of PDMB yields a truly atactic PME. This, however, should not be taken as a demonstration that the heterogenous hydrogenation of a polydiene will always yield a Bernoullian polyolefin.

Careful analysis of our ^{13}C NMR data indicates that the reduction of PDMB to PME was at least 99.7%. No evidence was found for the presence of head-to-head/tail-to-tail additions in the PME polymers. This observation serves to fortify the conclusion reached by Morton and Falvo[3] that 4,1-addition is the sole mode of monomer incorporation in the polymerization of 2-methyl-1,3-pentadiene. It should be noted that in the polymerization of

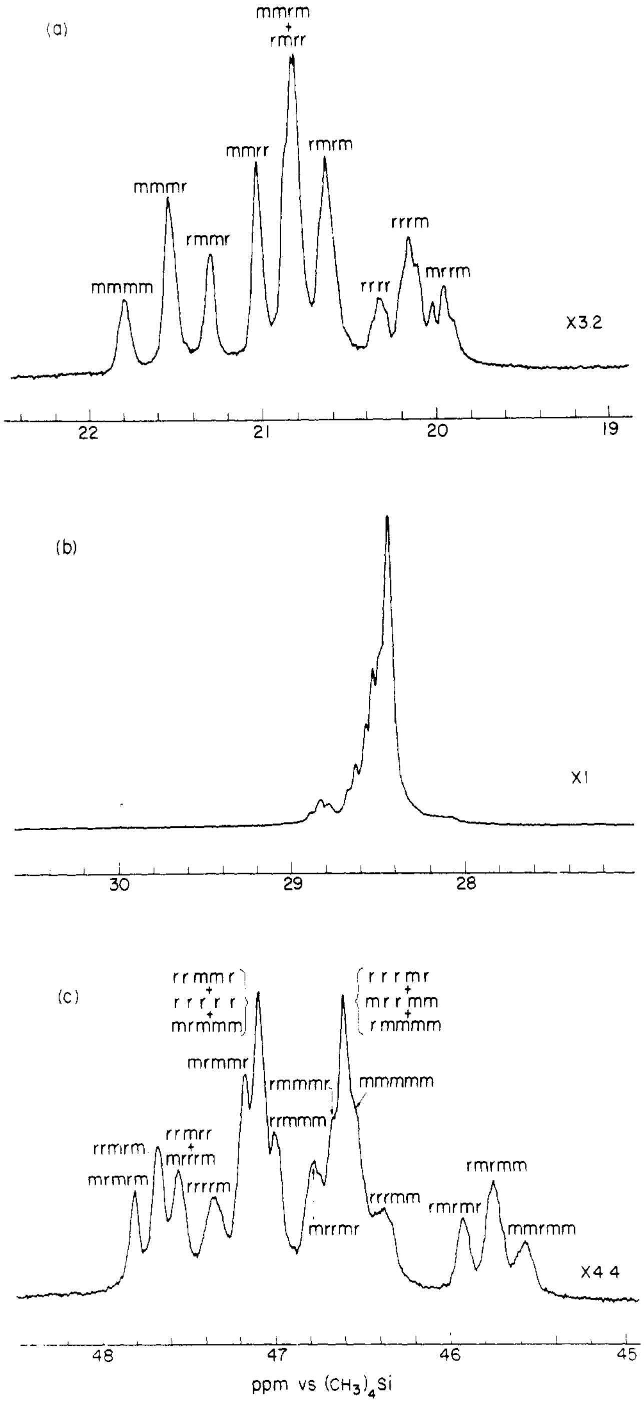

Figure 2. 50.31-MHz ^{13}C NMR spectra for the methyl (a), methine (b), and methylene (c) regions of PME-H in 1,2,4-trichlorobenzene–*p*-dioxane-d_8 at 110 °C.

Table III
Molecular Characteristics of Poly(methylethylene)

PME sample	$M_w \times 10^{-4}$	$[\eta]^{30\,°C}_{THF}$, dL g^{-1}	$[\eta]^{37.6\,°C}_{2\text{-octanol}}$, dL g^{-1}	M_z/M_w[a]	M_w/M_n[a]	k_H[b]
A	3.91	0.48_0	0.26_0	1.03	1.04	0.75
B	4.37	0.50_7	0.27_9	1.04	1.06	0.58
D	6.35	0.60_7	0.33_0	1.03	1.06	0.62
F	12.6	1.05	0.46_3	1.05	1.06	0.98
G	18.9	1.33	0.58_3	1.10	1.12	0.80
H	37.1	2.10	0.77_3	1.08	1.10	1.14

[a] Via the Waters 150C size exclusion chromatograph. [b] θ conditions.

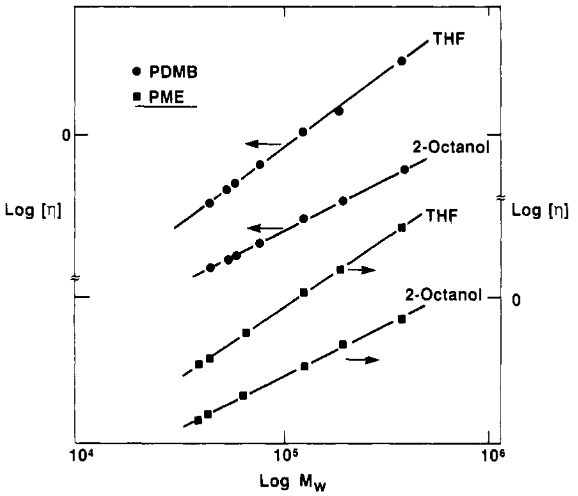

Figure 3. Log-log plot of $[n]$ and M_w for PDMB and PME.

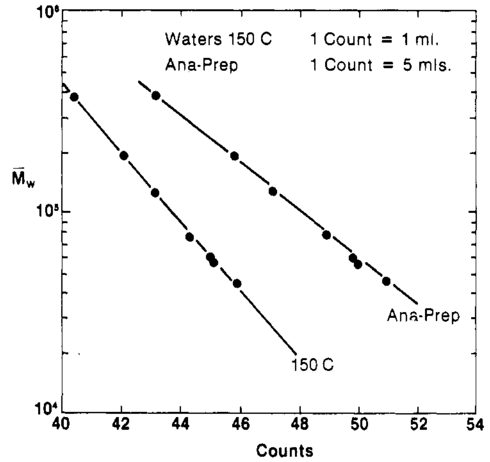

Figure 4. Size exclusion chromatography calibrations for PDMB.

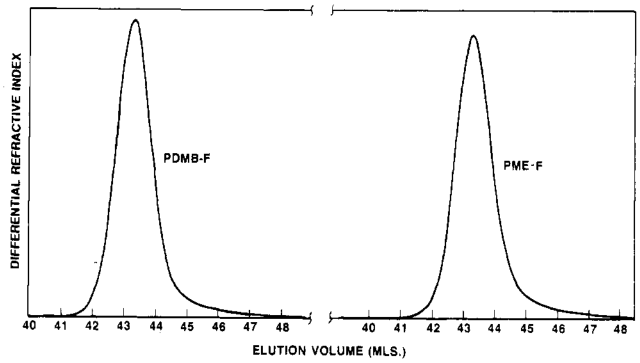

Figure 5. Size exclusion chromatographs for PDMB-F and PME-F.

propylene via the vanadium-based catalysts these irregular linkages are frequently observed.[16-18] In contrast, head-to-head/tail-to-tail defects are not usually observed in isotactic PME's produced by titanium catalysts.[19]

Characteristic Ratios. Determination of Flory's characterist ratio[20] can be done by the combination of intrinsic viscosity measurements and weight-average molecular weights. Measurements in nonideal solvents require the use of extrapolation procedures[21,22] while measurements under Θ conditions yield directly the unperturbed chain dimensions. The latter approach was used in this work, with 2-octanol being the Θ solvent.

The ratio $\langle r^2\rangle_0/M_w$ is obtainable from the relation[23,24]

$$[\eta]_\Theta = \Phi(\langle r^2\rangle_0/M_w)^{3/2}M_w^{1/2} = K_\Theta M_w^{1/2} \qquad (1)$$

where the unperturbed mean-square end-to-end distance is denoted by $\langle r^2\rangle_0$, $[\eta]_\Theta$ is the Θ temperature intrinsic viscosity in dL g^{-1}, and Φ is the Flory constant.[24-26] The value of this constant, $2.5(\pm 0.1) \times 10^{21}$, is based on measurements under Θ conditions on a variety of narrow molecular weight distribution polymers.[10,27-32]

The intrinsic viscosity measurements for both polymers were done with tetrahydrofuran and 2-octanol. The $[\eta]$ and M_w data of Tables II and III and Figure 3 yield the following relations for PDMB:

$$[\eta]^{30°C}_{THF} = 2.47 \times 10^{-4}M_w^{0.71} \qquad (2)$$

$$[\eta]^{28.9°C}_{2\text{-octanol}} = 1.12 \times 10^{-3}M_w^{0.50} \qquad (3)$$

$$[\eta]^{30°C}_{THF} = 4.60 \times 10^{-4}M_w^{0.66} \qquad (4)$$

$$[\eta]^{37.6°C}_{2\text{-octanol}} = 1.38 \times 10^{-3}M_w^{0.50} \qquad (5)$$

The validity of molecular weights assigned to the PDMB samples is demonstrated by the coherent calibrations obtained by combining the absolute values of M_w and the SEC peak retention time for each sample (Figure 4). Similar behavior was found for the PME materials. The near-monodisperse character of the samples used in this study is demonstrated by the PDMB and PME chromatograms of Figure 5.

The parameter involving $\langle r^2\rangle_0$ and molecular weight is obtained from Flory's equation

$$K_\Theta = \Phi(\langle r^2\rangle_0/M_w)^{3/2} \qquad (6)$$

Hence, for PDMB (in Å)

$$\langle r^2\rangle_0^{1/2} = 0.765M_w^{1/2} \qquad (7)$$

while the corresponding relation for PME is

$$\langle r^2\rangle_0^{1/2} = 0.820M_w^{1/2} \qquad (8)$$

The characteristic ratio, C_∞, can then be calculated from the following:

$$C_\infty = \lim_{n\to\infty}\left[\frac{\langle r^2\rangle_0/M_w}{(n'/M)l^2}\right] \qquad (9)$$

where n is the number of bonds in the chain and n' denotes the number of backbone chain bonds per repeat unit, l is the mean-square average bond length, and M is the monomer molecuar weight. The values of l used are those given by Abe and Flory.[33] Table IV contains the values K_Θ and C_∞.

Table IV
Unperturbed Chain Parameters for Poly(1,3-dimethyl-1-butenylene) and Poly(methylethylene)

	PDMB	PME
$K_\Theta \times 10^{3}$ [a]	1.12[b] (1.11)[c]	1.32[b] (1.35)[c]
C_∞	5.5 (5.5)	5.8 (5.9)

[a] From measurements under Θ conditions. [b] Via the Mark-Houwink-Sakurada plot. [c] Via the Burchard-Stockmayer-Fixman extrapolation procedure.[21,22]

The characteristic ratio for PDMB of 5.5 is similar to those found for poly(1-methyl-1-butenylene) (5.1 and 5.3)[9,34] and poly(1-butenylene) (5.1),[9] which have roughly equivalent microstructures. These combined experimental results fortify Mark's[35] conclusion, based on the rotational isomeric state (RIS) approximation, that the addition of a methyl group to the poly(1-butenylene) chain will exert little influence on C_∞ as long as the polydiene is not classifiable as a high-trans material. Our results for PDMB show that the presence of methyl groups on alternate carbons also fails to influence the polydiene chain posture to a significant extent. This, though, would not be the expected[35] result for the case of a high-trans polydiene since methyl substitution will cause an attenuation in the population of the relatively compact gauche states.

The use of the RIS approach has led[36-39] to calculated values of C_∞ for atactic PME. The most refined of these is the five-state approach by Suter and Flory,[37] which leads to a value of about 5.5 at 140 °C and higher values at lower temperatures. Our experimental value for PME at a temperature of 38 °C in combination with the calculated Suter-Flory value indicates that the temperature coefficient of the chain dimensions possesses a negative sign and is relatively small. This conclusion is in general agreement with the indication from the calculations of Suter and Flory[37] that $\mathrm{d}\ln C_\infty/\mathrm{d}T$ can assume a value of $<-1 \times 10^{-3}$ deg^{-1}.

Our results indicate that the preferrd conformational parameters for atactic PME (from those listed in Table VI of the Suter-Flory paper) are as follows: E_η = 60-70 cal mol^{-1}, E_τ = 500 cal mol^{-1}, E_ω = 1.2-1.5 kcal mol^{-1}, η = 1.05-1.07, τ = 0.4, and ω = 0.7-0.9, where E_τ and τ were constant. The parameters η, τ, and ω are factors entering into the elements of the statistical weight matrices.

Our experimental value of 5.9 for the PME characteristic ratio can be compared with the previously available values,[40,41] which range from 5.4 at 153 °C to 6.8 at 34 °C. Two points can be made as possible explanations for the case where discrepancies exist; to wit, our PME is a truly atactic material (P_m = 0.502) resulting from a direct synthetic approach and is devoid of head-to-head/tail-to-tail placements. As has been mentioned, such structures can occur[16-18] in certain preparations of PME from propylene. A secondary feature of our samples is that their near-monodisperse molecular weight distributions remove the need to correct K_Θ for polydispersity effects. Failure to do so for polydisperse materials can lead to ambiguity in the resultant value of the characteristic ratio.

The Huggins coefficients under Θ conditions (Tables II and III) show, for the higher molecular weight samples, values close to one. This behavior has been observed[9-12] previously for various near-monodisperse polydienes and polyolefins. To the best of our knowledge, this behavior is not explained by current theories,[42-44] with one possible exception.[45] Although not listed, the corresponding values for the Huggins constants in tetrahydrofuran were in accord with the predictions[46,47] that $k_H \leq 0.4$ in good solvents.

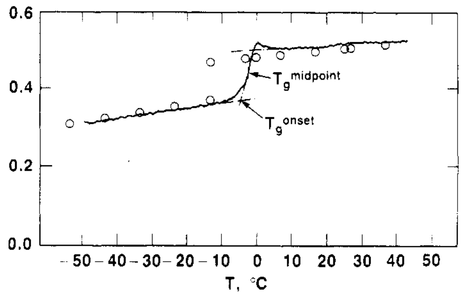

Figure 6. Heat capacity as a function of a temperature for sample PME-F. The positions of T_g(onset) and T_g(midpoint) are shown. The circles represent values of C_p as tablulated by Gaur and Wunderlich.[49]

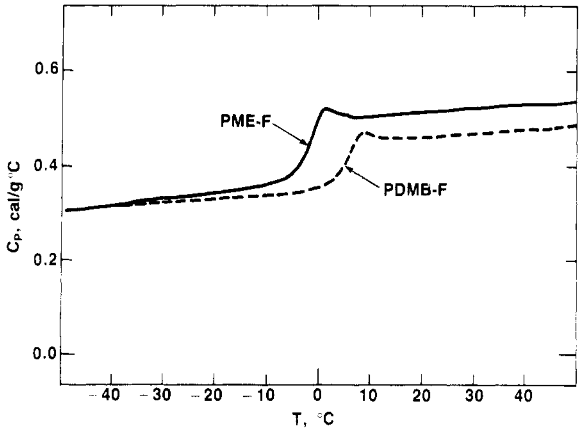

Figure 7. Heat capacity as a function of temperature for PDMB-F (dashed line) and PME-F (solid line).

Table V
Glass Transitions and Heat Capacity Changes of Poly(1,3-dimethyl-1-butenylene) and Poly(methylethylene)

sample	$M_n \times 10^{-4}$ [a]	T_g(onset), °C	T_g(midpoint), °C	ΔC_p, cal g^{-1} °C^{-1}
PDMB-B	4.15	1.1	3.7	0.103
PDMB-D	5.50	2.2	4.5	0.100
PDMB-F	11.7	2.6	4.7	0.104
PDMB-G	16.6	2.2	4.5	0.097
PDMB-H	34.6	2.3	4.1	0.096
PME-B	4.08	-8.0	-6.1	0.127
PME-D	5.99	-5.3	-3.6	0.130
PME-F	11.8	-4.5	-2.6	0.127
PME-G	16.7	-4.2	-2.0	0.126
PME-H	33.4	-4.6	-2.4	0.129
PP-I	*b*	-20.3	-18.0	0.089
PP-J	6.0	-10.4	-7.5	0.140

[a] The M_n values of the PME samples were calculated with the heterogeneity indices available in Tables II and III. The M_n value for PP-J was determined by size exclusion chromatography (Waters 150C) where the columns were calibrated with the PME samples of Table III. [b] SEC measurements yielded an apparent M_n of ca. 10^3.

Thermal Properties. The thermal behavior of all PDMB and PME samples was examined by differential scanning calorimetry. Temperatures at the onset of the glass transition and at the midpoint of the heat capacity jump, $\Delta C_p = C_p(\text{liquid}) - C_p(\text{glass})$, were determined graphically and with the aid of the computer programs available with the Perkin-Elmer thermal analysis data system. Values obtained in this way at a scan rate of 10 °C/min are reported in Table V (see also Figures 6 and 7). Note the small endothermic peak near 4 and 9 °C in Figures 6 and 7, respectively. This peak was present in every sample. It is due to the sample overshooting the equilibrium liquidus line during the heating cycle.[48] This endotherm was eliminated in the calculation of ΔC_p by extrapolation of linear portions of the glassy and liquid C_p and T_g (dashed lines in Figure 6). ΔC_p was measured at T_g (midpoint) between the extrapolated glassy and liquid specific heats. The T_g of sample PME-F was also noted at heating rates of 0.31, 0.62, 1.25, 2.5, and 5 °C/min. Decreasing the scan rate to 0.31 °C/min lowered T_g approximately 3 °C. Sample PME-F was also heated to 200 °C and no additional transitions, such as the melting of crystalline sequences, were noted.

Two other samples made by the direct polymerization of propylene were included in our study. Sample PP-I is a low molecular weight commercial material described as amorphous polypropylene (Hercules AFAX 600 HL-5). Sample PP-J is a research sample from Hercules that was fractionated by Plazek (see ref 49). The T_g's at the midpoint for these two samples were −18 and −7.5 °C. Gaur and Wunderlich[50] have reported that the average value for the T_g of atactic polypropylene is −13 °C.

The glass transition of our samples with molecular weights above 6×10^4 is approximately −2.5 °C and hence considerably higher than T_g for PME obtained from other sources. We do not know all of the causes of this difference but the following are likely to be contributing factors: (1) tacticity differences (the amorphous poly(methylethylenes) examined to date have not had the ideal (Bernoullian) atactic structure); (2) head-to-head and tail-to-tail defects (some catalyst systems used to polymerize propylene cause this type of error in monomer placement): we have found that the material obtained by the hydrogenation of poly(1,2-dimethyl-1-butenylene) exhibits a T_g(midpoint) of −25 °C; comonomer impurities (often commercial poly(methylethylenes) contain small amounts of other α-olefins such as ethylene[51]); (4) low molecular weight species (some PME samples have a high concentration of low molecular weight polymer or other contaminants; e.g., see PP-I in Table V). Specifically, we believe that factors 1 and 4 contribute to the low T_g of PP–I and that factor 3 has lowered the T_g of PP-J. These factors could account for the diversity of T_g values for "atactic" PME that are tabulated elsewhere.[52]

Sample PME-F was also studied to determine its heat capacity. The measured values of C_p(glass) are about 1.0% lower than the tabulated data of Gaur and Wunderlich for amorphous polypropylene as derived from 20 various "atactic", isotactic, and syndiotactic specimens.[50] From 10 to 50 °C C_p(liquid) is about 2.5% higher than the reference data. Below T_g the effect of crystallinity and tacticity differences on the C_p of polystyrene and poly(methyl methacrylate) was found to be 1% or less.[53,54] However, above T_g and below T_m these C_p differences can be large (>10%). Thus, one would expect good agreement between the glassy C_p in the present work and the older data even though the latter samples contain some degree of crystallinity.

Comparison of our glassy and liquid C_p measurements with the data of Dainton and co-workers on "atactic" polypropylene (crystallinity $\simeq$16%) shows our data are approximately 0.9% lower than theirs below T_g and above T_g their data appear to be influenced by premelting.[55] From −50 to +50 °C Passaglia and Kevorkian report C_p values for "atactic" PME (crystallinity $\simeq$3%) that are 2.2% lower than the values of the present work.[56] ΔC_p at T_g for ref 55 and 56 is 0.109 and 0.114 cal g^{-1} °C^{-1}, respectively.

The average value of ΔC_p at T_g in this work is 0.128 ± 0.002 cal g^{-1} °C^{-1} (Table V). This value agrees well with the extrapolated difference in heat capacity between the melt and the crystal at T_g as reported in ref 50 (0.134 cal g^{-1} °C^{-1}). However, this value is substantially larger than the tabulated value of C_p(liquid) − C_p(glass) at T_g of 0.104 given in the same reference for amorphous poly(methylethylene). Apparently, the earlier reported values of ΔC_p are anomalously low due to the presence of crystals that are always present even after solvent extraction in nonideal atactic samples.[55,56] Likewise, the crystallinity model used to derive C_p for glassy and crystalline polypropylene is not completely satisfactory in predicting the polymer's thermal behavior.[50]

It is hoped that future studies on the polymers we have prepared and on well-characterized PME made by direct polymerization of propylene will address the question of why the thermal properties of the two polymers differ. The use of pure propylene monomer and fractionated samples would eliminate factors 3 and 4 and allow a proper assessment of effects due to tacticity and head-to-head and tail-to-tail defects.

The heat capacity of PDMB-F was also measured (see Figure 7). Its T_g is approximately 7 °C higher than that of PME-F and the heat capacity jump is only 0.104 cal g^{-1} °C^{-1}. Note that the hydrogenation and conversion of PDMB to atactic polypropylene results in an increase of flexible bonds in the polymer's backbone from three to four. O'Reilly[57] and DiMarzio and Dowell[58] have shown that the methyl groups in propylene can be neglected in calculating the specific heat at T_g. From theory ΔC_p for propylene is predicted to be 0.122 cal g^{-1} C^{-1}.[58] If we reduce the configurational C_p terms in the DiMarzio–Dowell theory for PME by 25%, which corresponds to the loss in flexible bonds in going from PME to PDMB, ΔC_p is calculated to fall from 0.122 to 0.097. Our experimental ΔC_p values of 0.128 and 0.100 ± 0.02 cal g^{-1} °C^{-1} for PME and PDMB, respectively, are in good agreement with this predicted thermal behavior for the two polymers. A small amount of this C_p difference seems to manifest itself some 10–20 °C before the onset of the glass transition.

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Registry No. Poly((*E*)-2-methyl-1,3-pentadiene) (homopolymer), 26714-20-5; polypropylene (homopolymer), 9003-07-0.

References and Notes

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Effects of Cationic Surfactants on the Conformation of Poly[(*S*)-(carboxymethyl)-L-cysteine]

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ABSTRACT: The induction of the β-structure of fully neutralized poly[(*S*)-(carboxymethyl)-L-cysteine] in solution depends markedly on the head groups of cationic surfactants. It occurs only on the addition of dodecylammonium chloride (DAC) but not by the addition of dodecyldimethylammonium chloride (DDAC) or dodecyltrimethylammonium chloride (DTAC), as revealed by circular dichroism. Infrared absorption spectra of the precipitates produced by the addition of an excess amount of each of the three surfactants show that the polypeptide assumes the β-structure in the complexes with DAC or DDAC, but that the random coil conformation is dominant in the complex with DTAC. The intensity of a characteristic absorption band of the carboxylate group around 1585 cm^{-1} in the complexes with surfactants is vanishingly weak for DDAC, weak for DAC, but very strong for DTAC. Decrease of pH in salt-free solutions occurs on addition of the surfactants in the order DAC > DDAC > DTAC. The effects of ionic strength and polypeptide concentration on the induction of the β-structure differ markedly from those found on the induction of the α-helix of poly(L-glutamic acid) by the same surfactants.

Introduction

The interaction of ionic surfactants with ionic polypeptides has been studied extensively.[1-12] However, the effects of different head groups on the interaction have received less attention than those of different hydrocarbon chain lengths. It was found in a recent study that the α-helix of poly(L-glutamic acid) (PGA) was induced by three cationic surfactants that had different head groups but a common hydrocarbon tail.[13] Marked differences were observed among these three surfactants when they were added to an extent more than required to induce the α-helix, while a small difference was found among their inducing powers.

In the present study, the effects of the three surfactants used in the previous study,[13] dodecylammonium chloride (DAC), dodecyldimethylammonium chloride (DDAC), and dodecyltrimethylammonium chloride (DTAC), on the conformation of poly[(*S*)-(carboxymethyl)-L-cysteine] (poly[Cys(CH$_2$COOH)]) are examined by circular dichroism (CD) in solution and by infrared absorption (IR) in the solid state. In the light of recent characterizations of the β-structure of poly[Cys(CH$_2$COOH)],[14-16] the β-structure found in the present study is most likely (although not confirmed) to consist of aggregates of folded chains.

Experimental Section

The weight-average molecular weight and the degree of polymerization of the sample of poly[Cys(CH$_2$COOH)] used in the present study were 5.8 × 10^4 and 360, respectively. Some characterizations of the sample were given in a previous report.[16] The

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