NOTES

Effect of Tacticity on Chain Entanglement in Poly(methyl methacrylate)

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Chain entanglement is a key concept in the dynamics of polymer chains.[1-3] Recently, we have shown that the entanglement junction is a binary hooking contact between two chains.[4] The entanglement density is thus shown to be controlled by chain tortuosity, and increases as the chain tortuosity increases.[4-6] The chain tortuosity is affected by the rotational conformational states of chain segments, which are in turn affected by the tacticity of a chain. Therefore, chain entanglement behavior should vary with chain tacticity.

In this work, we show that the plateau modulus G_N^0 and the entanglement molecular weight M_e of poly(methyl methacrylate) (PMMA) are indeed profoundly dependent on chain tacticity.

EXPERIMENTAL

Materials

All conventional samples of PMMA were prepared by free-radical polymerization, as described before.[7] The syndiotactic-rich, isotactic-rich, and narrow molecular-weight distribution samples were obtained from Polysciences, Inc., Warrington, Pennsylvania 18976–2590, U.S.A.

The molecular weight and its distribution were determined by gel permeation chromatography. The tacticity was determined by NMR (500 MHz, $CDCl_3$ solution at 25°C). The triad fractions mm (isotactic), mr (atactic) and rr (syndiotactic) were read from the NMR spectra, and the diad fractions m (meso) and r (racemic) were then calculated from the triads fractions by the first order Markov statistics.[8] The characteristics of all samples are summarized in Table I.

Dynamic Viscoelastic Spectroscopy

The linear-viscoelastic dynamic shear storage modulus G' and loss modulus G'' were measured by sinusoidal oscillation with small strains (generally 0.5 to 5%) as a function of frequency and temperature in the melt, using Rheometrics Mechanical Spectrometer System IV. The G' and G'' master curves were obtained by time–temperature superposition.

It is usually difficult to accurately determine the entanglement plateau modulus G_N^0 by traditional methods, since dynamic modulus or creep compliance curves do not become really flat in the plateau zone, unless the polymer

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sample has very high molecular weight and narrow molecular weight distribution.[9]

However, this difficulty can be avoided by using the recently developed and more widely applicable relationship[7,10-15]

$$G_N^0 = [G']_{\tan\delta\to\text{minimum}} \qquad (1)$$

where G_N^0 is the entanglement plateau modulus, and $\tan\delta$ is the loss tangent. That is, G_N^0 is equal to G' at the frequency where $\tan\delta$ is at a minimum in the plateau zone.

This method, i.e., eq 1, has recently been extensively verified[7] and graphically illustrated.[15] It has been shown that the G_N^0 value thus determined is invariant with respect to molecular-weight and molecular-weight distribution,[7] and is equal to the G_N^0 value determined by the integration of G'' curve of PMMAs and polystyrenes.[7,15] The G_N^0 values determined by eq 1 are usually reproducible within about 5—10%.

In this work, we have thus determined the plateau modulus G_N^0 by eq 1 from the dynamic storage modulus G' at the frequency where $\tan\delta$ is at a minimum in the plateau zone. The G_N^0 values thus determined for the present samples have probable uncertainties of about 5—10%.

It should be noted that if a sample contains appreciable amounts of fractions having molecular weights below the entanglement value, the G' value at the minimum of $\tan\delta$ is an apparent G_N^0 value. The true G_N^0 value is greater than the apparent value, and can be obtained by[7,9]

$$G_N^0 = (G_N^0)_{\text{ap}}/v_p^2 \qquad (2)$$

where $(G_N^0)_{\text{ap}}$ is the apparent plateau modulus (i.e., the G' value at the minimum of $\tan\delta$), and v_p the volume fraction of the polymer having molecular weights above the entanglement value.

In this work, however, all polymer samples used have sufficiently high molecular weights without appreciable amounts of fractions having molecular weights below the entangle-

ment value. Therefore, the true plateau moduli were obtained directly from the dynamic moduli without needing a correction using eq 2.

The entanglement molecular weight M_e is related to G_N^0, and calculated by[9]

$$M_e = \rho RT/G_N^0 \qquad (3)$$

where ρ is the mass density at temperature T at which the plateau modulus G_N^0 was measured, and R the gas constant. The melt density ρ data were taken from the literature.[16]

RESULTS AND DISCUSSION

Plateau Modulus

Table I lists the weight-average molecular weight $\bar{M}_w$, polydispersity ratio, $\bar{M}_w/\bar{M}_n$, the plateau modulus G_N^0, the temperature of measurement, the diad and triad tacticity fractions, and the molecular weight between entanglement points M_e for five conventional, one syndiotactic-rich, and one isotactic-rich samples. It can be seen that G_N^0 and M_e vary with the tacticity.

We have previously shown that, in statistical copolymers, the plateau modulus follows the geometric-mean relationship.[7] A heterotactic chain may be considered as a statistical copolymer of meso and racemic units. We thus have

$$\log G_N^0 = m\log(G_{Nm}^0) + r\log(G_{Nr}^0) \qquad (7)$$

where G_{Nm}^0 is the plateau modulus of pure isotactic polymer, and G_{Nr}^0 that of pure syndiotactic polymer.
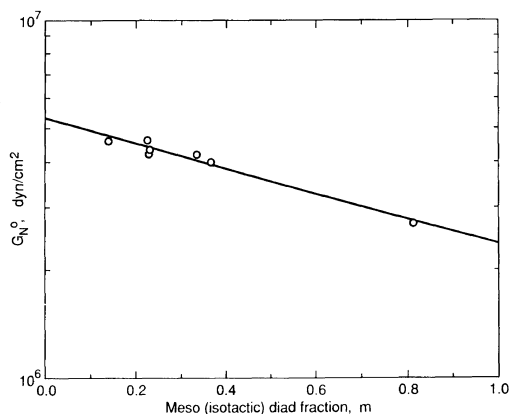
Figure 1 shows $\log G_N^0$ versus the fraction of meso (isotactic) diads. The solid line is obtained by least-squares regression, given by

$$\log G_N^0 = m\log(2.4\times10^6) + r\log(5.3\times10^6) \qquad (8)$$

where G_N^0 is in dyn cm^{-2} at $180°C$, and the standard deviation of regression is only $\pm3\%$. Equation 8 adequately expresses the dependence of plateau modulus on tacticity. Thus, the plateau modulus of pure isotactic

Table I. Plateau modulus G_N^0 and entanglement molecular weight M_e of PMMA

$\bar{M}_w/$ kg mol^{-1}	$\bar{M}_w/\bar{M}_n$	$T/°C$	$G_N^0/$ dyn cm^{-2}	Diads		Triads			$M_e/$ g mol^{-1}
				m	r	mm	mr	rr	
Narrow molecular-weight distribution polymer:									
115	1.11	190	4.2×10^6	0.23	0.77	0.02	0.42	0.56	10200
Conventional free-radical polymers:									
123	1.75	180	4.6×10^6	0.23	0.77	0.04	0.37	0.59	9100
96.4	1.90	160	4.2×10^6	0.33	0.67	0.10	0.46	0.43	9600
84.4	1.91	144	4.0×10^6	0.37	0.63	0.14	0.45	0.41	10100
2860	3.91	180	4.3×10^6	0.23	0.77	0.04	0.37	0.58	9800
Syndiotactic-rich polymer:									
92.7	2.49	180	4.6×10^6	0.14	0.86	0.02	0.24	0.74	9100
Isotactic-rich polymer:									
346	3.84	140	2.7×10^6	0.81	0.19	0.74	0.15	0.11	14200

Figure 1. log G_N^0 versus fraction of meso (isotactic) diads in poly(methyl methacrylate)s. The symbols are experimental. The line is by least-squares regression, i.e., eq 8, with a standard deviation of $\pm 3\%$.

polymer is $G_{Nm}^0 = 2.4 \times 10^6$ dyn cm^{-2}, and that of pure syndiotactic polymer is $G_{Nr}^0 = 5.3 \times 10^6$ dyn cm^{-2}.

The maximum atactic fraction which can exist in a heterotactic chain occurs at diad fractions $m = r = 0.5$. In order words, an "ideal" (maximally) atactic polymer has triad fractions of $mm = rr = 0.25$, and $mr = 0.5$. Therefore, the plateau modulus of an "ideal" (maximal) atactic polymer is $G_{Na}^0 = 3.5 \times 10^6$ dyn cm^{-2}.

Conventional PMMAs usually have diad

fractions in the range from $m = 0.2$, $r = 0.8$ to $m = 0.4$, $r = 0.6$, corresponding to $G_N^0 = 4.5 \times 10^6$ to 3.8×10^6 dyn cm^{-2}, respectively. The "typical" free-radical PMMA is usually quoted to have $m = 0.25$ and $r = 0.75$, corresponding to $G_N^0 = 4.3 \times 10^6$ dyn cm^{-2}. These are summarized in Table II.

Entanglement Molecular Weight

The entanglement molecular weight M_e is calculated from G_N^0 by eq 3, and listed in Table I.

Analogous with eq 7, we can express the dependence of entanglement molecular weight on chain tacticity as

$$\log M_e = m \log(M_{em}) + r \log(M_{er}) \quad (9)$$

where M_{em} is the entanglement molecular weight for pure isotactic polymer, and M_{er} that for pure syndiotactic polymer. Least-squares regression gives

$$\log M_e = m \log(1.7 \times 10^4) + r \log(7.9 \times 10^3) \quad (10)$$

for PMMA. Figure 2 plots $\log M_e$ versus m, wherein the symbols are experimental, and the solid line is the least-squares regression line, given by eq 10.

Table II. Plateau modulus and entanglement molecular weight *versus* tacticity of PMMA[a]

Polymer	Diads		$\rho/$ $\mathrm{g\,ml^{-1}}$ 180°C	$G_N^0/$ $\mathrm{dyn\,cm^{-2}}$	$M_e/$ $\mathrm{g\,mol^{-1}}$
	m	r			
Stereoregular polymers:					
Pure isotactic	1	0	1.120	2.4×10^6	17000
Pure syndiotactic	0	1	1.114	5.3×10^6	7900
Maximal atactic	0.5	0.5	1.116	3.5×10^6	13000
Conventional free-radical polymers:					
"Typical"	0.25	0.75	1.115	4.3×10^6	9800
"Low" isotactic	0.2	0.8	1.114	4.5×10^6	9300
"High" isotactic	0.4	0.6	1.117	3.8×10^6	11000

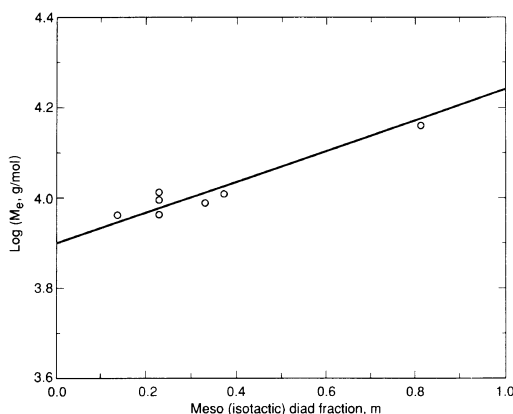[a] G_N^0 values calculated by eq 8 with standard deviation $\pm 3\%$.

Figure 2. $\log M_e$ *versus* fraction of meso (isotactic) diads in poly(methyl methacrylate)s. The symbols are experimental. The line is by least-squares regression, given by eq 10, with a standard deviation of $\pm 3\%$.

Table II summarizes the M_e values for pure syndiotactic, pure isolactic, "ideal" (maximal) actactic, and typical conventional PMMAs.

Comparison with Previous Work

Masuda and coworkers[17,18] measured the linear viscoelastic dynamic shear storage and loss moduli for an extensive series of PMMAs having very high molecular weights and narrow molecular-weight distribution. Their curves show well-defined plateau regions between better than any other previous work, and therefore have been widely disseminated. It is notable that our value of $M_e = 9800$ is

Table III. Summary of entanglement molecular weight for conventional poly(methyl methacrylate), determined from dynamic shear modulus[a]

M_e	Investigator/s	Ref
9800	Wu and Beckerbauer	This work
9640 ± 2100	Masuda, *et al.* (1970, 1972)	17, 18
9130	Wu (1987)	11
7000	Han and Kim (1989)	19
6200	Lomellini and Rossi (1990)	14

[a] Average value: $M_e = 8400 \pm 1500$.

quite close to their value of 9640 ± 2100.

Table III lists the literature values of M_e determined from dynamic shear modulus by various workers[11,14,17-19] for conventional PMMAs, giving an average values of $M_e = 8400 \pm 1500$, consistent with our present value.

Very recently, Lu and Jiang[20] have just published a set of characteristic ratio C_∞ values determined by intrinsic viscosity $[\eta_0]_\theta$ measurement for PMMAs as a function of tacticity. Their C_∞ data can be used to calculate the M_e values, which can then be compared with our M_e values determined from G_N^0 data, as follows.

The length of an entanglement strand is determined by chain tortuosity, given by[4]

$$N_v = 3C_\infty^2 \qquad (11)$$

where N_v is the number of real and/or virtual skeletal bond which is the elementary con-

Table IV. Comparison of C_∞ and M_e values for stereoregular PMMAs: this work from G_N^0 *versus* latest work of Lu and Jiang from $[\eta_0]_\theta$[a]

Meso diads	C_∞	C_∞	M_e	M_e
$m = (mm)^{1/2}$	From $[\eta_0]_\theta$ of Lu and Jiang	From G_N of this work by eq 12	From C_∞ of Lu and Jiang by eq 11	From G_N^0 of this work by eq 3
0	7.4	7.3	8200	7900
0.1	7.7	7.5	8900	8500
0.1	7.8	7.5	9100	8500
0.14	8.1	7.7	9800	8800
0.17	8.8	7.7	12000	9000
0.2	8.9	7.8	12000	9200
0.39	9.7	8.6	14000	11000
0.53	9.9	8.9	15000	12000
0.94	10.3	10.3	16000	16000
0.96	10.3	10.5	16000	16500

[a] The C_∞ values of Lu and Jiang were determined from $[\eta_0]_\theta$ data, taken from Lu and Jiang.[20]

formational rotational unit, and C_∞ the characteristic ratio of the coiled chain. Note that $M_e = N_v M_v$, where M_v is the average molecular weight per real and/or virtual skeletal bond. Therefore, M_e can be calculated from C_∞ by eq 11, *i.e.*, $M_e = 3M_v C_\infty^2$. We have listed the C_∞ values determined from $[\eta_0]_\theta$ by Lu and Jiang, and used them to calculate the M_e values by our eq 3, as listed in Columns 2 and 4 of Table IV, respectively.

Furthermore, the characteristic ratio can be calculated from the entanglement molecular weight by $C_\infty = (M_e/3M_v)^{1/2}$, or from the plateau modulus by

$$C_\infty = \{\rho RT/(3M_v G_N^0)\}^{1/2} \qquad (12)$$

obtained by combining eq 3 and 11. We have listed our M_e values determined from G_N^0, and used them to calculate the C_∞ values by eq 12, as listed in Columns 3 and 5 in Table IV, respectively.

It can be seen that the C_∞ amd M_e values as a function of chain tacticity, determined by the two completely different experimental methods (*i.e.*, intrinsic viscosity $[\eta_0]_\theta$ and plateau modulus G_N^0) are in excellent agreement.

Recently, we have also developed a group

contribution method by which both the characteristics ratio C_∞ and the entanglement molecular weight M_e can be predicted from chemical structure and main-chain tacticity.[21]

SUMMARY AND CONCLUSIONS

We have shown that plateau modulus G_N and entanglement molecular weight M_e of PMMA are strongly dependent on tacticity, although they are independent of molecular weight and its distribution (in the absence of fractions with molecular weights below the entanglement value). The dependency on tacticity follows the geometric-mean (semilogarithmic) relationship with respect to diad fractions.

The plateau modulus G_N^0 and entanglement molecular weight M_e (the molecular weight of an entanglement strand) vary from 2.4×10^6 dyn cm^{-2} and 16400 for pure isotactic chains to 5.3×10^6 dyn cm^{-2} and 7800 for pure syndiotactic chains. $\log G_N^0$ and $\log M_e$ vary linearly with diad fractions. Conventional free-radical polymers have meso (isotactic) diad fractions of 0.2 to 0.4 and racemic (syndiotactic) diad fractions of 0.8 to 0.6, and have G_N^0 and M_e ranging from 4.4×10^6

dyn cm^{-2} and 9600 to 3.9×10^6 dyn cm^{-2} and 11000, respectively.

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