Bulk Properties of Poly(macromonomer)s of Increased Backbone and Branch Lengths

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ABSTRACT: We measured dynamic shear moduli of poly(macromonomer)s of an increased backbone chain length and those bearing branch chains of increased branch length up to the critical molecular weight for the intermolecular chain entanglement, M_c, of a linear polystyrene as functions of frequency and temperature using a parallel-plate rheometer. The poly(macromonomer)s were prepared from ω-methacryloyloxyethyl polystyrene macromonomers (MA-PSt)s or ω-vinylbenzyl polystyrene macromonomers (VB-PSt)s. It was revealed that a great increase in the backbone length caused the poly(macromonomer)s to show a weak rubbery plateau region in the master curves of the storage modulus G', where the molecular weights of the branch chains were smaller than M_c. The plateau modulus was much lower than that observed for the linear polystyrenes. On the other hand, the poly(macromonomer)s with polystyrene branches are nearly equal to the M_c, and a very short backbone chain showed a clear rubbery plateau region. The glass transition temperature of poly(macromonomer)s in the region without the chain entanglement decreased with decreasing branch length but remained almost constant over the wide range of the backbone length.

Introduction

The effect of branching architecture on the polymer molecular properties is an important and fundamental subject. Construction of branching architecture of polymer molecules with long branches is performed via many routes, such as (a) termination methods—coupling method of living polymers with a multifunctional compounds;[1−3] (b) initiation methods—living polymerizations with multifunctional initiators or radical polymerizations with side-chain-type macroinitiator;[4,5] and (c) the arm-first method—sequential anionic block copolymerization of the first monomer with a divinyl compound as the second monomer.[6,7]

In addition to these, chain polymerizations of vinyl-terminated macromonomers easily produce multibranched polymers of extremely high branch density.[8−13] The branch length and the branch number can be controlled by the molecular weight of the macromonomer and the polymerization conditions. Thus, poly(macromonomer)s are very interesting model polymers for investigation on the effect of branching architecture. In fact, it has been revealed that poly(macromonomer)s show very unique and interesting molecular and bulk properties associated with the branching architecture.[14−23]

On the other hand, rheological properties of branched polymers, such as star polymers, comb-shape polymers, and H-shape polymers have been investigated by many researchers for a long time.[24−29] However, the effects of the branched structure on the rheological properties are still not well understood. In the previous paper, we reported the rheological properties of poly(macromonomer)s having a particular branch length.[30] The number-average molecular weight M_n of the branch was 2740. This molecular weight is lower than the critical molecular weight for the intermolecular chain entanglement, M_c, of a linear polystyrene. The data showed that the intermolecular chain entanglement coupling was suppressed in the poly(macromonomer)s in the melt state due to the multibranched structure. Recently, Vlassopoulos et al. also pointed out the suppression of the chain entanglement in the poly(macromonomer)s.[31] In this paper, we further investigated the influence of increase in the backbone or branch length on the intermolecular chain entanglement couplings and the glass transition temperature. It was shown that a great increase in the backbone length caused the poly(macromonomer)s to show a weak rubbery plateau region in the master curves of the storage modulus G'. The glass transition temperature of poly(macromonomer)s in the region without the chain entanglement decreased with decreasing in the branch length but remained almost constant over the wide range of the backbone length.

Experimental Section

Materials. Syntheses of ω-methacryloyloxyethyl polystyrene macromonomers (MA-PSt)s of different molecular weights and ω-vinylbenzyl polystyrene macromonomer (VB-PSt)s were carried out by living anionic polymerization of styrene with *s*-BuLi followed by addition of ethylene oxide and termination with methacryloyl chloride or vinylbenzyl chloride.[9,10] These macromonomers were polymerized with azobis(isobutyronitrile) (AIBN) in benzene at 50−60 °C with different macromonomer concentrations. Polymerization products were purified by precipitation−extraction procedures with cyclohexane−petroleum ether mixed solvents to remove unreacted macromonomer. The purification was repeated several times until the sharp peak in the gel permeation chromatograph (GPC), corresponding to the unreacted macromonomer, com-

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Table 1. Characteristics of Poly(macromonomer)s for Dynamic Mechanical Property Measurements

sample code	total			backbone		wt % of backbone chain[c]	branch	
	M_w[a] ($\times 10^{-6}$)	M_n[a] ($\times 10^{-6}$)	M_w/M_n	M_w ($\times 10^{-3}$)	DP[b]		M_w ($\times 10^{-3}$)	M_w/M_n
poly(MA-PSt1070)-763	1.06	0.886	1.20	76.3	763	10.6	1.39	1.30
poly(MA-PSt1070)-2600	3.61	2.96	1.22	260	2600	10.6	1.39	1.30
poly(MA-PSt1070)-7390	10.3	8.43	1.21	739	7390	10.6	1.39	1.30
poly(MA-PSt2300)-1030	2.75	2.27	1.21	103	1030	4.9	2.66	1.15
poly(MA-PSt2300)-3640	9.67	8.40	1.15	364	3640	4.9	2.66	1.15
poly(MA-PSt2300)-7094	18.9	16.7	1.13	709	7094	4.9	2.66	1.15
poly(MA-PSt2740)-397[d]	1.372	0.759	1.81	39.7	397	4.1	3.45	1.26
poly(MA-PSt2740)-2545[d]	8.780	5.624	1.56	255	2545	4.1	3.45	1.26
poly(MA-PSt3500)-2700	10.8	8.87	1.22	270	2700	3.2	4.00	1.14
poly(MA-PSt18400)-14	0.325	0.309	1.05	1.41	14.1	0.61	23.0	1.24
poly(MA-PSt18400)-74	1.70	1.58	1.08	7.40	74	0.61	23.0	1.24
poly(VB-PSt45600)-9	0.491	0.434	1.13	0.848	9	0.25	57.9	1.27

[a] Molecular weights of poly(macromonomer)s were determined using GPC equipped with a low-angle laser light scattering detector. [b] DP is based on the weight-average molecular weight. [c] Calculated from the fraction of the methacryloyloxyethyl group using M_n of the corresponding macromonomers. Use of M_w gives the value for poly(MA-PSt2740)s as 3.3%. [d] From ref 30.

pletely disappeared. The purification−isolation procedure improved the molecular weight distribution of the poly(macromonomer)s.

The weight-average molecular weight, M_w, and the polydispersity index, M_w/M_n, of the macromonomers were determined by GPC (Tosoh HLC802A/LS-8) with a calibration curve constructed using polystyrene (PSt) standards. Those of poly(macromonomer)s were determined by the GPC using a low-angle laser light scattering (LALLS) detector and a refractive index (RI) detector.[9] The GPC was operated with Tosoh G5000H-G3000H columns on chloroform at 35 °C. Recent investigation on the chain tacticity of poly(MA-PSt)s showed that the central polymethacrylate backbone chain of the poly(macromonomer)s here have similar tactic structure to that of poly(methyl methacrylate) (PMMA) prepared by conventional free radical polymerizations.[32]

Measurement of Dynamic Mechanical and Thermal Properties. Dynamic mechanical properties of the polymer samples in the melt were measured using the Bohlin CSM rheometer with a parallel plate geometry under nitrogen atmosphere. Disk samples of 24 mm diameter were prepared for the rheological measurements by a hot press at 160 °C, using polymer powder samples obtained by freeze-drying with benzene. The rheological measurements were carried out in the angular frequency range 0.1−100 s^{-1} and the temperature range 120−220 °C. The film-forming property was investigated in connection with the rheological data. The film specimens were prepared by solvent casting of toluene solution of each sample onto slide glasses at room temperature (20 °C). The glass transition temperature, T_g, of poly(macromonomer)s was determined using a Rigaku-DSC8230 and Perkin-Elmer 7 series thermal analysis systems. The T_g of linear polystyrene standards was also measured for comparison. The sample (ca. 2 mg) was heated from 0 °C or room temperature to 150 °C at a heating rate of 10 °C/min. The T_g was determined from the second scan curves.

Results and Discussion

Effect of the Long Backbone with Short Branches on Viscoelastic Behavior. Polymerization of vinyl-terminated macromonomers like MA-PSt and VB-PSt produces multibranched polymers of extremely high branch density. The branch number is as high as >1000; thus, molecular bottle-brush-like poly(macromonomer)s are formed as shown in Figure 1. On the other hand, the poly(macromonomer)s of a short backbone chain with long branches behave approximately as star-branched polymers in another extreme case. This depends on the molecular weight of the original macromonomer and the polymerization conditions. The number of branches of the poly(macromonomer)s for the dynamic shear moduli measurement is in the range 10−7000, which is equivalent to the degree of polymerization, DP, of the poly(macromonomer)s. The molecular characteristics of the poly(macromonomer)s used for the measurements of dynamic mechanical properties are shown in Table 1.

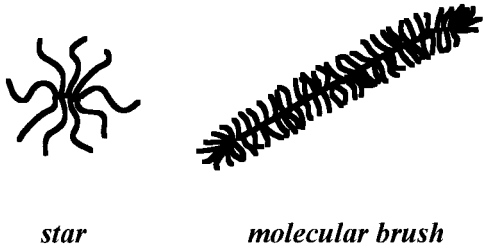

Figure 1. Schematic representation of poly(macromonomer)s.

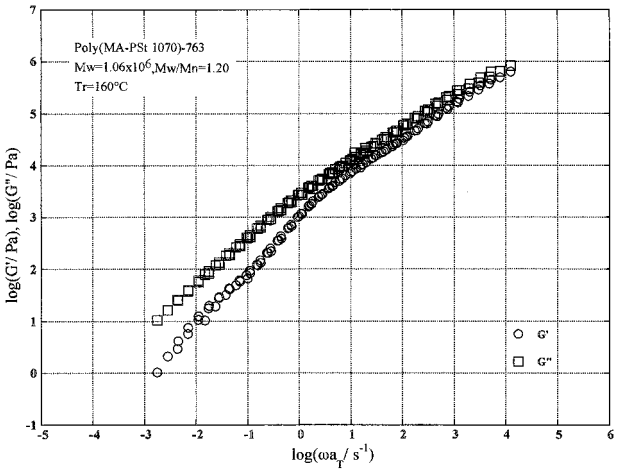

Figure 2. Master curves of G' and G'' of poly(MA-PSt1070)-763 at T_r = 160 °C.

Figure 2 shows the master curves of the dynamic shear moduli, G' and G'', for the poly(macromonomer), poly(MA-PSt1070)-763, constructed at a reference temperature T_r = 160 °C, assuming the time−temperature superposition principle for G' and G'' data measured at different temperatures. The temperature dependences of the shift factors were represented by the WLF equation for this and all other poly(macromonomer)s as reported in the previous paper.[30] The molecular weight of the polystyrene branches of this poly(macromonomer) is lower than the M_c of linear polystyrenes.[33,34] The average DP of the polymethacrylate backbone chain is 763. The molecular weight of PMMA corresponding to the polymethacrylate backbone is 7.63×10^4, which is larger than the M_c of linear atactic poly(methyl meth-

Table 2. Plateau Modulus and M_e of Poly(macromonomer)s

sample code	G_N^0 (Pa)[a] (A)	G_N^0 (Pa)[a] (B)	$M_e \times 10^{-3}$ [b] (A)	$M_e \times 10^{-3}$ [b] (B)	film-forming property
poly(MA-PSt 1070)-7387	2.88×10^3	3.02×10^3	1250	1190	good
poly(MA-PSt 2300)-7094	1.50×10^3	1.91×10^3	2410	1890	rather good
poly(MA-PSt 2740)-2313	1.26×10^3	1.72×10^3	2860	2090	brittle
poly(MA-PSt 3500)-2700	1.10×10^3	1.06×10^3	3272	3410	brittle
poly(MA-PSt18400)-74	2.09×10^5	2.63×10^5	17.2	21.4	good
poly(VB-PSt45600)-9	2.00×10^5	1.68×10^5	18.0	23.0	good

[a] G' value in the plateau region: (A) at midpoint in the plateau region; (B) at the minimum point in tan δ curve. [b] Calculated from G' value in (A) and (B) using the equation $G_N^0 = (\rho RT/M_e)$.

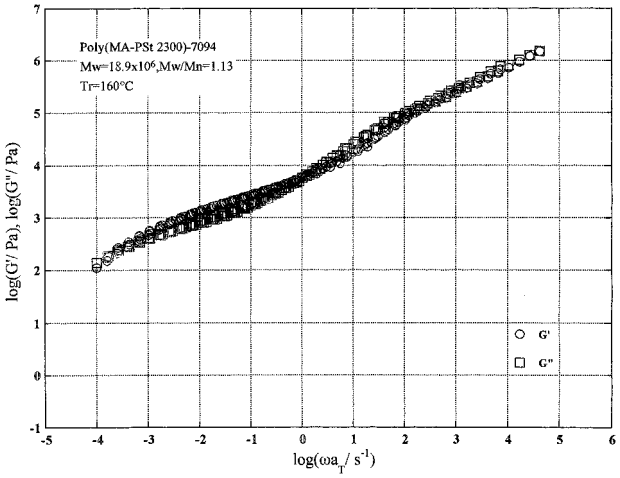

Figure 3. Master curves of G' and G'' of poly(MA-PSt2300)-7094 at $T_r = 160$ °C.

acrylate)s (PMMA)s ($M_c = 2M_e$).[34−36] It is seen from Figure 2 that G' as well as G'' monotonically decreases from the edge of the glass transition zone and directly goes to the terminal zone with decrease in the frequency, and there is no rubbery plateau region. This behavior is very similar to those of the poly(macromonomer) in the previous paper. As the backbone length increases, a weak shoulder appears which becomes more clear with further increase in the backbone chain length.

Figure 3 shows the master curves of the G' and G'' for poly(MA-PSt2300)-7094 constructed at the reference temperature, $T_r = 160$ °C. The number-average molecular weight of the polystyrene branches of this poly(macromonomer) is lower than M_c for linear polystyrene again, but the molecular weight of PMMA corresponding to the polymethacrylate backbone chain is 7.094×10^5, which is much larger than M_c of a linear PMMA. In Figure 3, there appears a weak but clear plateau region in G' where the frequency dependence of G' is small and the value of G' is greater than G''. The appearance of the plateau region indicates the elastic nature in the poly(macromonomer) melt, which suggests some kinds of chain entanglement couplings between the poly(macromonomer) molecules.

The plateau modulus seen in Figure 3 is much lower than those of linear PMMAs, polystyrenes, and the copolymer in the previous paper.[30] Entanglement spacing, i.e., the molecular weight between the two entanglement coupling loci, M_e, can be estimated using the relation $M_e = \rho RT/G_N^0$, where G_N^0 is the plateau modulus.[34] The M_e becomes 2.41×10^6 when G_N^0 is evaluated at the midpoint in the plateau region. When G_N^0 is evaluated at the minimum point of tan δ in the plateau region, the M_e is estimated to be 1.89×10^6. The value of M_e are extremely larger than that of a linear PMMA. These values of M_e for this and other poly(macromonomer)s are summarized in Table 2.

Table 3. Molecular Weight between Two Entanglement Coupling Loci (M_e) of Various Methacrylate Polymers

polymer	$M_e \times 10^{-3}$	ref
poly(methyl methacrylate)	5.9 (110 °C)	34
	9.2 (180 °C)	35
	10.0 (140 °C)	37
poly(*tert*-butyl methacrylate)	28.1 (−)	35
poly(*n*-hexyl methacrylate)	33.9 (100 °C)	34
poly(4-*tert*-butylphenyl methacrylate)	69.7 (−)	36
poly(diphenylmethyl methacrylate)	74.1 (−)	36
poly(*n*-octyl methacrylate)	87.0 (100 °C)	34
poly(*n*-dodecyl methacrylate)	155 (25 °C)	35
poly(triphenylmethyl methacrylate)	203 (−)	36
poly(MA-PSt)s	1250−3270 (160 °C)	this work

M_e of linear polymers in the melt state is related to the polymer molecular structure. For example, the M_e of methacrylate polymers increases with increasing in the size of the ester group as shown in Table 3. Among these polymers, poly(triphenylmethyl methacrylate) with the isotactic chain structure can form a helical structure due to the bulky triphenylmethyl group and gives large M_e value. However, the M_e values of poly(macromonomer)s are much larger than that of poly(triphenylmethyl methacrylate). We consider that M_e is related to the molecular cross-sectional area, A_c, of the polymer molecules. The increase in A_c may cause increase in M_e of polymers of the same chain length, because the increase in A_c tends to exclude other molecules in a unit volume. The specific multibranched structure of the poly(macromonomer)s should increase A_c greatly. This may be a reason for the very large M_e of the poly(macromonomer)s. Recently, Fetters et al. discussed on the universal relationship between the entanglement molecular weight and the molecular characteristics for linear polymers.[38,39] They showed that the M_e and also M_c of wide range of linear polymers were well described by using the packing length, p, of the polymer molecule. The M_e is related to the p by

$$M_e = \rho RT/G_N^0 = n_t N_A \rho p^3 \quad (1)$$

where n_t is constant, ρ is the polymer melt density, and N_A is the Avogadro number.[38] Since the values of the end-to-end distance of the poly(macromonomer)s in Table 1 were not measured, we could not discuss the values of M_e for the poly(macromonomer)s with the p so far. However, the packing length is the increasing function of the molecular cross-sectional area. This also indicates the large value of the M_e of the poly(macromonomer)s.

Recent investigation on the poly(macromonomer)s revealed that the multibranched structure with the very

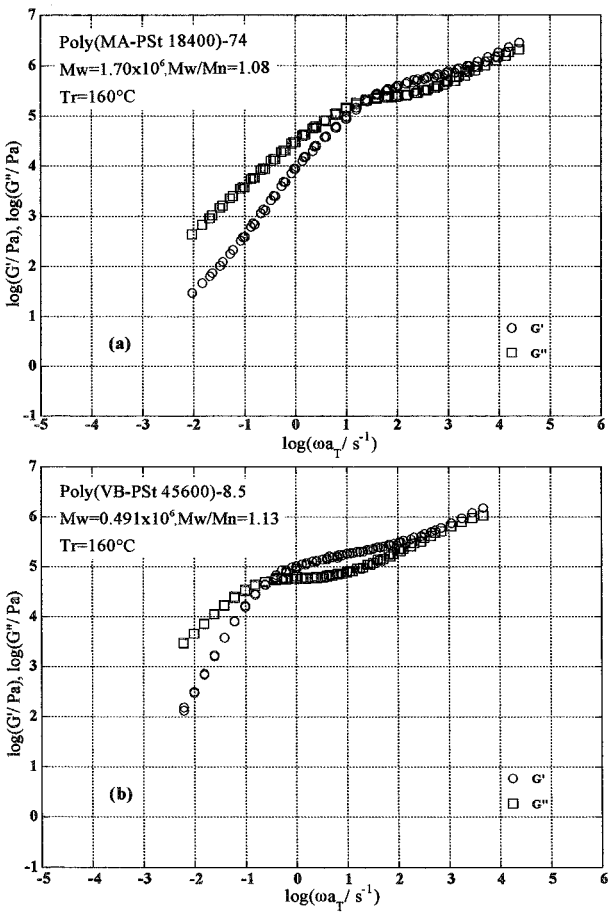

Figure 4. (a) Master curves of G' and G'' of poly(MA-PSt18400)-74 at $T_r = 160$ °C. (b) Master curves of G' and G'' of poly(VB−PSt45600)-9 at $T_r = 160$ °C.

high branch density created marked repulsive interaction between PSt branch chains in the poly(macromonomer)s, which strongly affected the chain stiffness of the backbone chain and the molecular conformation in solution.[14,18−23] This effect is so strong that the poly(macromonomer)s can form mesomorphic phase in solution depending on the branching architecture.[20,22,23] This molecular feature is maintained in bulk and can affect the intermolecular coupling of poly(macromonomer)s. The increased chain stiffness may prevent the intermolecular entanglements in the manner of binary hooking as usually assumed in the case of the flexible linear polymers. The relationship between the M_e and the chain stiffness parameter, i.e., the Kuhn's statistical segment length, and also the packing length of the poly(macromonomer)s are interesting to study and actually now under investigation.

Effect of the Branches around M_c. Parts a and b of Figure 4 show the master curves of G' and G'' for the poly(macromonomer)s of poly(MA-PSt18400)-74 and poly(VB−PSt45600)-9, respectively. For the poly(macromonomer) bearing the largest molecular weight branches in this study, the polymerizable end group of the original macromonomer was changed to a vinylbenzyl one. As the molecular weight of the MA-PSt macromonomer increases, the ceiling temperature strongly influences the polymerization reaction and results in the low conversion and in the extreme case results in no formation of poly(macromonomer)s. The weight fraction of the central backbone chain in the poly(VB-PSt45600) is 0.25, and the rest is polystyrene branches. Thus, the influence of the difference in the backbone chain is minor. The poly(macromonomer) from the VB-PSt45600 macromonomer has less than 10 branches as the average; thus, this poly(macromonomer) is nearly a star-branched polymer with polystyrene branches approximately equal to the M_c of linear polystyrenes.

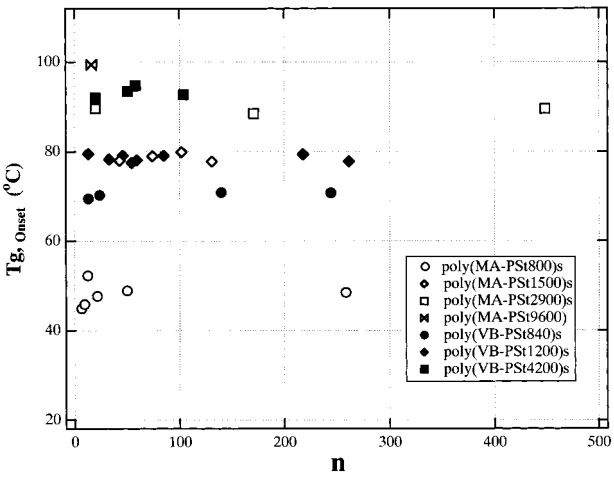

Figure 5. Glass transition temperature of poly(macromonomer)s plotted against the number of branches (n).

In Figure 4, in marked contrast to the poly(macromonomer)s in Figures 2 and 3, there is a clear plateau region in each master curve of G', although the backbone chain is short. From the plateau modulus in Figure 4, the entanglement spacing M_e is estimated as 17 000−23 000. This value is very close to the M_e values for linear polystyrenes in the literature,[33,34] indicating that the rubbery plateau region is related to the chain entanglement coupling between the polystyrene branch chains of different poly(macromonomer) molecules. It is very interesting to note that M_w of the original macromonomer of poly(MA-PSt18400)-74 in Figure 4 is 23 000 and $M_w/M_n = 1.24$. This means that the branch chain length of poly(MA-PSt18400)-74 is longer than M_e but still rather smaller than the M_c of linear polystyrenes where linear polystyrenes cannot entangle with each other. Despite this, poly(MA-PSt18400)-74 and also poly(MA-PSt18400)-14 in Table 1 show a clear plateau region. This suggests that the topological factor related to the multibranched structure can influence the chain entanglement by increasing the relaxation time of branch chains to unravel the entanglement. Moreover, it is also possible that the branching structure of the poly(macromonomer)s influences the $M_c = 2M_e$ relationship known for the conventional linear polymers.[38] Since the relaxation time, τ_b, of a branch chain of star polymers increases exponentially with the ratio of the molecular weight of the branch chain M_b to the M_e as[40]

$$\tau_b \propto M_b^{3/2} \exp(\nu M_b/M_e) \qquad (2)$$

it may be possible that a great increase in the branch length of poly(macromonomer)s creates extremely strong intermolecular entanglement coupling due to the multibranched structure with very high branch density.

Glass Transition Temperature. Finally, the influence of the chain lengths of the backbone and the polystyrene branches on the glass transition temperature, T_g, was investigated. T_g of poly(macromonomer)s as functions of the chain lengths of the backbone and branch chain is shown in Figure 5. All of these poly(macromonomer)s bear the polystyrene branches shorter

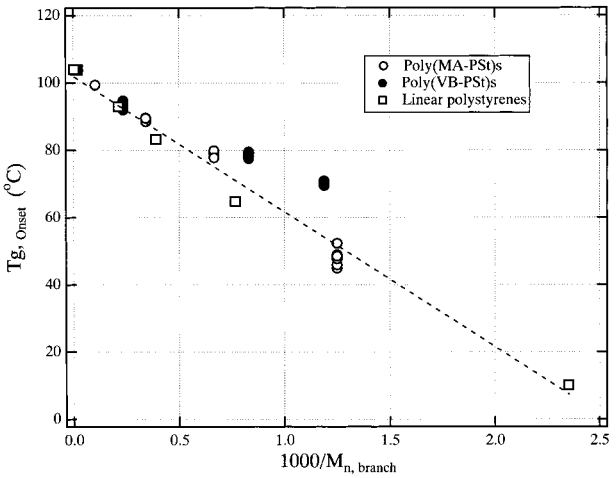

Figure 6. Glass transition temperature of poly(macromonomer)s plotted against the number of chain ends per unit molecular weight. Data of linear polystyrenes are also included. The dotted line is calculated from curve fitting of the linear polystyrene data using the eq 3.

than the M_c. Figure 5 demonstrates that T_g of poly(macromonomer)s depends on the branch length, where T_g decreases with decrease in the branch length. However, T_g is independent of the number of branches; that is, T_g is almost constant over the wide range of the backbone length. This behavior is very reasonable if we consider the chain end effect of the polystyrene branches through the excess free volume around the chain ends. The number of the chain end per unit molecular weight changes with the branch length, but it remains constant against the change in the number of branches, because the branch length is uniform and predetermined by the molecular weight of the original macromonomer. This can be seen from Figure 6 where T_g is plotted against the chain end density in the molecule.[41] The T_g data for linear polystyrenes are also included for comparison taking account of two chain ends per molecule. When the chain entanglement is absent, the molecular weight dependence of T_g is simply expressed by eq 3[42,43]

$$T_g = T_g^{\infty} - (\theta_e \rho N_A/\alpha) n_e/M_n = A - B/M_n \qquad (3)$$

where θ_e is the excess free volume per chain end, n_e is the number of chain ends per molecule, ρ is the density of the polymer, and N_A is Avogadro's number. $(\theta_e \rho N_A/M_n)n_e$ in eq 3 is the excess free volume associated with the chain ends per unit volume. The dotted line in Figure 6 is calculated by curve fitting of the eq 3 for linear polystyrene data which gave $A = 375$ and $B = 4.02 \times 10^4$. Deviation of the T_g data of poly(VB-PSt)s from linear polystyrenes is seen at the high chain end density region, while the data of poly(MA-PSt)s are almost on the dotted line. This difference may be ascribed to the influence of the backbone chain. Because the molecular weight of the branch chain decreases, the weight fraction of backbone chain increases.This effect should depend on the chemical structure of the backbone chain, and actually it is seen in Figure 6.

Conclusion

It was shown from the dynamic shear moduli data that a great increase in the backbone chain length creates the intermolecular chain entanglement couplings in the poly(macromonomer) systems, where the entanglement density is very low due to the multibranched structure of high branch density. On the other hand, increase in the branch chain length causes the branch chains to entangle intermolecularly, where M_e is almost similar to that of linear polystyrenes. In the latter case, the branched structure promotes rather than prevents the entanglement coupling. These findings are also consistent with the film-forming property of the poly(macromonomer)s. T_g of poly(macromonomer)s does not simply depend on the molecular weight as in the case of linear polymers. The branch length strongly influences T_g, but the increase in the molecular weight of the poly(macromonomer)s by increase in the branch number does not change T_g.

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