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Critical Solution Point and Chain Dimension of Branched-Polystyrene Solutions

Shinobu Sato, Mamoru Okada, and Takuhei Nose*

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku,
Tokyo 152, Japan

Summary

Critical solution point and chain dimension were measured for branched polystyrene(BPS) in solution as a function of molecular weight(M) and compared with those for linear polystyrene(LPS). The critical concentration ϕ_c of BPS was quite different from that of LPS at a fixed M, but the same at a fixed overlap-concentration ϕ^*, i.e., plots of ϕ_c vs. ϕ^* fall on a single straight line for both BPS and LPS ($\phi_c \propto \phi^*$). Reduced critical temperature τ_c defined by $\tau_c \equiv (\Theta - T_c)/\Theta$ [T_c : critical temperature, Θ : the Θ-temperature] was related to ϕ_c as $\tau_c \propto \phi_c{}^{\sim 2}$ for BPS, whereas $\tau_c \propto \phi_c$ for LPS.

Introduction

Recently de Gennes(1) pointed out that the critical concentration of polymer solutions ϕ_c is of the order of overlap concentration ϕ^*. If it is so, a branched polymer should have different ϕ_c from that of a linear polymer at a fixed molecular weight because of difference in chain dimension. Nakano(2) measured the phase diagram for linear and branched polyethylenes in diphenylether, and found that the corporation of branches depressed the precipitation temperature compared at the same molecular weight. Kajiwara et al.(3) also found for randomly-crosslinked polystyrene that the location of the spinodals was hardly affected with regard to temperature though the crosslinking had increased the molar mass, which implies the depression of the phase separation temperature by crosslinking compared at the same molecular weight. More recently, Daoud et al.(4) presented a theory for the phase diagram of randomly-branched polymers on the basis of scaling arguments. The critical concentration ϕ_c and the reduced critical temperature τ_c (defined as $(\Theta - T_c)/\Theta$) are given by the theory as

$$\phi_c \sim \phi^* \sim N^{1-\nu d} \qquad (1)$$

$$\tau_c \sim N^{\nu d-2} \qquad (2)$$

accordingly,

$$\tau_c \sim \phi_c{}^{\frac{\nu d-2}{1-\nu d}} \qquad (3)$$

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* To whom all correspondence should be addressed

where Θ is the Θ-temperature, T_c the critical temperature, N the degree of polymerization, d the spacial dimension, and ν the index for N-dependence of the radius of gyration R_g : $R_g \propto N^\nu$. The index ν for randomly-branched polymers near Θ is 7/16, i.e., R_g is expressed as(4)

$$R_g = N^{7/16}\Lambda^{-1/16}\ell \tag{4}$$

Here, Λ is the fraction of branched points in a chain, and ℓ is the statistical segment length. From equation(1)-(3), therefore, the following relations are predicted for the randomly-branched polymer.

$$\phi_c \sim N^{-5/16} \tag{5}$$

$$\tau_c \sim N^{-11/16} \tag{6}$$

$$\tau_c \sim \phi_c^{11/5} \tag{7}$$

These results of equation (5)-(7) are in contrast with the behavior of linear polymers, that is, $\phi_c \sim \tau_c \sim N^{-1/2}$ predicted by equation (1)-(3) with d = 3 and $\nu = 1/2$. The depression of T_c observed for branched polyethylenes(2) and crosslinked polystyrene(3) is inconsistent with the theoretical prediction (equation (6)), and the finding that plots of T_c^{-1} against the reciplocal of intrinsic viscosity $[\eta]^{-1}$ fall on the same straight line for both the linear and branched polyethylenes seems to also conflict with the prediction of equation (7). (Note that $\phi^* \propto [\eta]^{-1}$) The shift of T_c to higher concentration by branching(3), however, suggests that equation (1) or (5) may hold.

In this work, we have measured ϕ_c, T_c and R_g for branched polystyrenes having different N and Λ in methylcyclohexane, and examine the above predictions for differences in ϕ_c and T_c between linear and branched polymers.

Experimental

Samples

Branched polystyrenes were prepared by copolymerization of styrene(ST) and p-divinylbenzene(DVB) with two different compositions, i.e., 1000/1 and 500/1 in mole ratio (The yield was 36.5% and 30.6%, respectively). The expected value of the fraction of branched points is 0.86×10^{-3} for [ST]/[DVB] =1000 and 1.64×10^{-3} for [ST]/[DVB] = 500 (see Appendix). The polymers obtained were fractionated using benzene and methanol.

Experimental Methods

The fractionated samples were characterized by light scattering and gel permeation chromatography (Toyo Soda HLC 803D; RI-8; LS-8). The light scattering measurements were carried out for the samples in t-decalin at 20.5°C (the Θ-temperature for linear polystyrene(5)) by a specially designed photometer using an argon-ion laser operating at 488 nm (6).

The weight average molecular weight M_w, R_g, and the second virial coefficient A_2 were obtained from angular- and concentration-dependences of scattered intensity. The refractive index increment used was 0.124 cm^3/g (7). The overlap concentration defined here as $\phi^* = M_w\bar{V}_p/(N_A R_g{}^3)$ was also calculated from the values of M_w and R_g obtained, where N_A is Avogadro's number and $\bar{V}_p$ the specific volume of polymer (0.95 cm^3/g).

For the branched polystyrenes in methylcyclohexane, cloud points were visually measured as a function of concentration, and the volume ratio of one separated phase to the other was also measured as a function of temperature below the cloud point. Critical point (ϕ_c, T_c) was determined as an intersection of the cloud point curve and the diameter at which the volume ratio is unity. The volume ratio obtained for different total concentrations approximately satisfied the lever rule, which implies no serious problem for polydispersity of the samples.

Results and Discussion

Numerical results of M_w, R_g, A_2, ϕ_c, and T_c are summarized in Table 1. Code numbers 10B and 5B denote the samples with the mole ratio of [ST]/[DVB] = 1000/1 and 500/1, respectively. Since A_2 in t-decalin is essentially zero at 20.5°C, this experimental temperature may be practically regarded as the Θ-temperature for the present samples.

Table 1. Various properties of branched polystyrene

		t-decalin**			methylcyclohexane	
Code No.	M_w / 10^4	R_g / nm	A_2 / ml mol/g^2	M_w/M_n*	T_c / K	ϕ_c / vol. fraction
10B1	946	60.6	-4.20×10^{-6}	1.12	340.2	0.035
10B2	323	40.0	3.65×10^{-7}	1.27	337.8	0.041
10B3	168	30.5	-6.82×10^{-6}	1.25	336.6	0.048
10B4	91	25.0	-4.14×10^{-6}	1.28	334.7	0.053
5B1	552	48.0	-2.67×10^{-6}	1.39	338.7	0.040
5B2	137	26.5	-9.98×10^{-6}	1.43	336.5	0.054
5B3	87	24.0	-1.01×10^{-5}	1.49	333.5	0.059
5B4	30	15.0	-3.82×10^{-6}	1.23	331.6	0.070

*determined by gel permeation chromatography
** at 20.5°C

Radius of Gyration

Fig. 1 shows double logarithmic plots of R_g against M_w, along with those for linear PS obtained by Inagaki et al. (5). Branched PS has a lower index of molecular weight dependence, i.e., $R_g \sim M_w{}^{0.38}$ for 10B series and $R_g \sim M^{0.40}$ for 5B series. These indices are consistent with the results for branched PS by Masuda et al.(8) and for branched low-density polyethylene by Hama et al.(9), but slightly smaller than the theoretical value 7/16 for a randomly-branched polymer (equation (4)). The dashed and dash-dotted lines in Fig. 1 indicate the theoretical values of equation (4) with the values of Λ estimated from the polymerization conditions (see Appendix) and ℓ = 0.308 nm which was evaluated from R_g for linear PS at the Θ-temperature(5) using the relation $R_g \cong N^{1/2}\ell$. Agreement between experiments and the theory is fairly good.

Critical Temperature

Fig. 2 shows double logarithmic plots of τ_c vs. M_w for linear(10) and branched PS's. Here, 69.76°C(10) was taken as the Θ-temperature for both linear and branched PS's. The branched PS has a slightly weaker molecular-weight-dependence of τ_c compared with linear PS for which $\tau_c \sim N^{\sim -0.5}$, and T_c is lower than that of linear PS at a fixed molecular weight, in accordance with previous experiments(2,3). These results conflict with the theoretical prediction of equation(6).

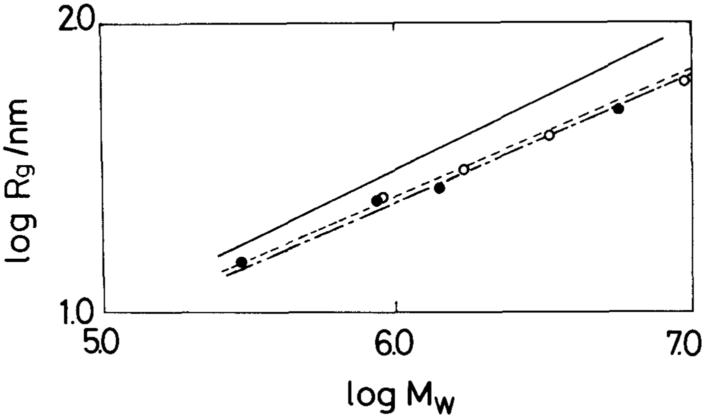

Fig. 1 Molecular weight dependence of R_g for branched PS [10B series (○); 5B series (●)] and linear PS (——)(5): theoretical curves for $\Lambda = 1.72 \times 10^{-3}$(----) and 3.27×10^{-3}(-·-·-) (equation(4)).

Critical Concentration

Difference in the molecular weight dependence of ϕ_c between branched and linear PS's is quite clear, as shown in Fig. 3. We have $\phi_c \sim M_w^{-0.18\sim-0.19}$ for branched PS with the dependence being weaker than equation(5), while $\phi_c \sim M_w^{-0.40}$ for linear PS(10), and the branched PS has a higher value of ϕ_c at a fixed M_w. However, Fig. 4 shows that the relation $\phi_c \propto \phi^*$ holds for both branched and linear PS, verifying the prediction of de Gennes, and moreover that the plots of ϕ_c vs. ϕ^* for both branched and linear PS's fall on the same straight line, i.e., the propotionality constant is the same. So, the branched and linear polystyrenes have the same value of ϕ_c at a fixed ϕ^* but not the same at a fixed M_w.

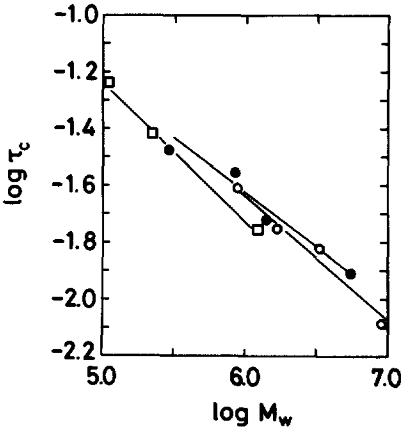

Fig. 2 Molecular weight dependence of τ_c for branched PS [10B series (○); 5B series (●)] and linear PS (□) (10).

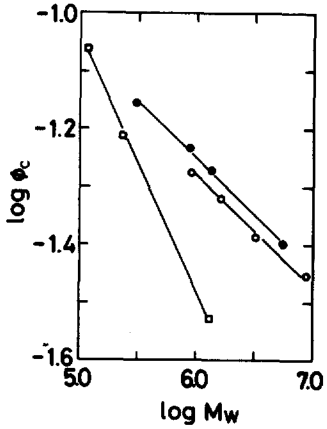

Fig. 3 Molecular weight dependence of ϕ_c for branched PS [10B series (○); 5B series (●)] and linear PS (□) (10).

Relation between ϕ_c and τ_c

Fig. 5 shows double logarithmic plots of τ_c against ϕ_c, exhibiting a quite different relation of τ_c vs. ϕ_c from that of linear PS. We have $\tau_c \sim \phi_c^{2.35}$ for 10B series and $\tau_c \sim \phi_c^{1.72}$ for 5B series. These findings conflict with the result of Nakano(2) for branched polyethylene which showed no difference in τ_c at the same value of ϕ^* between the linear and branched polymers, but are consistent with the theory (equation(7)). The quantitative agreement in the index with equation (7), however, is apparent, because the discrepancy of τ_c and ϕ_c from equation (5) and (6) was found as already mentioned.

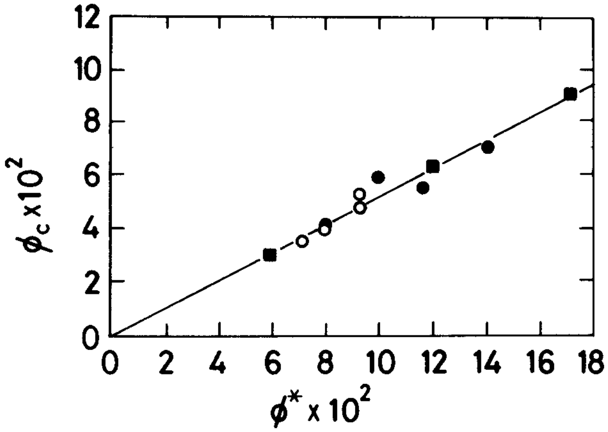

Fig. 4 Plots of ϕ_c vs. ϕ^* for branched PS [10B series (○); 5B series (●)] and linear PS (■) (10).

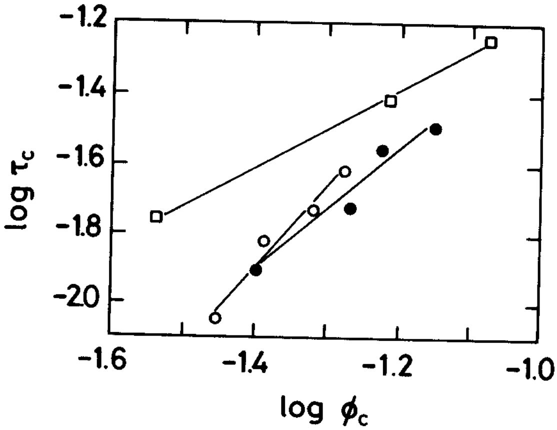

Fig. 5 Double logarithmic plots of τ_c vs. ϕ_c for branched PS [10B series (○); 5B series (●)] and linear PS (□) (10).

In conclusion, de Gennes' idea, $\phi_c \sim \phi^*$, has been verifyed for branched polystyrenes(ST-DVB copolymers), and it is found that the theory of Daoud et al. interprets differences in R_g, ϕ_c, and τ_c between branched and linear PS, but is not satisfactory to describe their behaviors quantitatively. It is not clear at this stage whether these quantitative disagreements come from theoretical falt or from that the samples are not ideal randomly-branched-polymers.

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Appendix

According to Wesslau(11), the fraction of branched points in a chain Λ is given for $m >> 1$ by

$$\Lambda = \frac{r_{12}(1-\alpha)^{2/r_{12}}/2 - r_{13}(1-\alpha)^{1/r_{13}} + r_{13} - r_{12}/2}{\alpha m(r_{13} - r_{12}/2)}$$

where m is the ratio of initial amount of styrene(ST) to that of p-divinylbenzene(DVB) in mole, α the yeild, r_{12} the reactive ratio of ST to DVB, and r_{13} the reactive ratio of ST to pendant double bond. We took $r_{12} = 0.15$ and $r_{13} = 1$ according to Dusěk (12). It should be noted that the value of Λ obtained does not exactly correspond to that in equation (4), since the copolymer of ST and DVB is not an ideal randomly-branched-polymer. So, in the calculation of R_g by equation (4) in Fig. 1, we tentatively took twice of these calculeded values for Λ, because one branched point has two branches in the present case.

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