Statistical Thermodynamic Treatment of Glass Transition for Cross-Linked Polymers of Varying Functionality

F. Rietsch

Laboratoire de Structures et Propriétés de l'Etat Solide, Université des Sciences et Techniques de Lille, 59650 Villeneuve d'ascq, France.

Received June 17, 1977

ABSTRACT: Measurements of glass transition temperature T_g have been done on "anionic" polystyrene networks and star-shaped polymers and show that the T_g depends closely on the average functionality of the cross-links. The results interpreted in terms of the statistical Gibbs–Di Marzio theory show that the effect of intermolecular interaction near the cross-links can explain the experimental results quite satisfactorily.

I. Introduction

In a recent study[1] of the glass transition temperature of cross-linked polystyrene networks prepared by anionic copolymerization of styrene and divinylbenzene (DVB)[2,3] in relation to the number average molecular weight $(\overline{M_n})$ between cross-links, we revealed a volume effect among different chains of the same nodule (DVB), linked to the functionality of the cross-link points. The experimental results obtained on cross-linked and star-shaped polymers, of known functionality, showed that this volume effect is all the greater the higher the functionality and can be linked to intermolecular interactions between polymeric segments near the cross-link nodules.[1]

Nevertheless, neither the free volume theory nor the statistical theory takes into account these interactions; for this reason, it is interesting to modify the statistical theory of Gibbs and Di Marzio[4-8] so as to make these intermolecular interactions apparent.

II. Linear Polymers

The Gibbs and Di Marzio[4-7] theory predicts the existence of a second-order transition at a uniquely defined temperature T_2 at which the system has only one degree of freedom, which requires that the configurational entropy vanishes. This temperature can be considered as being the limiting value of T_g on an infinite time scale.

For a quasicrystalline lattice containing a polymer phase consisting of n_x chains of size x and n_0 holes we have the following expressions, ref 4, eq 1, 11, and 22.

The intramolecular (flex) energy

$$E = f\epsilon_2(x-3)n_x + (1-f)\epsilon_1(x-3)n_x \qquad (1)$$

where f is the fraction of bonds in the orientation of energy ϵ_2. In this model the first two bonds of each molecule can be affected without changing the energy of the molecule.

For a lattice coordination number of four, the dependence of T_g on x is given by:

$$\frac{x}{x-3}\left\{\frac{\log v_1}{(1-v_1)} + \left(\frac{1+v_1}{1-v_1}\right)\log\left|\frac{(x+1)(1-v_1)}{2xv_1}+1\right| + \log\frac{3(x+1)}{x}\right\} = \frac{2\beta e^{\beta}}{1+2e^{\beta}} + \log(1+2e\beta) \qquad (2)$$

where $\beta = -\epsilon/kT$, k is the Boltzmann constant, v_1 is the free volume fraction at T_g, and $\epsilon = \epsilon_2 - \epsilon_1$ is the energy difference between rotational isomers in the chains.

The fraction of sites which are unoccupied, v_1, is related to E by:

$$\log\frac{v_1}{S_0{}^2} = \frac{2ES_x{}^2}{kT} \qquad (3)$$

for a coordination number of four, where $S_x = 1 - S_0$, $S_0 = 2v_1/(v_1+1)$, and $v_1 = n_0/(xn_x + n_0)$.

The difference in expansivities can be deduced from eq 3 and is given by (ref 8, eq 7)

$$T_g\Delta\alpha = \frac{v_1 \log|(v_1+1)^2/4v_1|}{2(1-v_1)/(1+v_1) - |4v_1/(1+v_1)|\log|(v_1+1)^2/4v_1| - (1-v_1)} \qquad (4)$$

Substituting experimental value $T_g(\infty) = 373$ K[9] and $\Delta\alpha = 4 \times 10^{-4}$ K^{-1} into eq 4, we obtain $v_1 = 0.046$, which is very far from the W.L.F. equation ($v_1 = 0.025$).[8,10]

A value of ϵ was calculated by eq 2 for polymer with $x \to \infty$. We obtain $\epsilon = 1.67 \times 10^{-21}$ cal/segment, whereas Gibbs[11] got $\epsilon = 1.52 \times 10^{-21}$ cal/segment. A better agreement with the experimental data, particularly for low values of x, is obtained with an earlier expression derived by Gibbs:[11]

$$\frac{1}{x-2}\left[\frac{v_1}{x(1-v_1)}\log v_1 - \log 2x + x - 1\right] = \frac{2e^{\beta}}{1+2e^{\beta}}\beta + \log(1+2e^{\beta}) \qquad (5)$$

In this model each chain is fixed in the lattice model by its finest segment so that every second segment has four vacant positions around the first. The remaining $N_2\,(x-2)$ segments are disposed according to the tetrahedral diamond lattice model.

The intramolecular energy is also given by:

$$E = f\epsilon_2(x-2)n_x + (1-f)\epsilon_1(x-2)n_x$$

Gibbs[11] found this relation in good agreement with the experimental data on polystyrene in the case of linear polymers.

In Figure 1, we have plotted the variation of T_g against x^{-1} in accordance with eq 5, making use of varying values of v_1 and ϵ. All those curves are similar but the closest agreement with the experimental values of T_g was obtained with the pair $v_1 = 0.022$ and $\epsilon = 1.555 \times 10^{-21}$ cal/segment. The initial slope is 3×10^5, notably higher than the experimental value[1] of 1.5×10^5, but agreement is satisfactory when the molecular weight $M_n < 20\,000$. In this way, Gibb's theory illustrates relatively well the behavior of linear chains of polystyrene of varying molecular weight. This figure shows too that the slope of the different curves is independent of ϵ and v_1, which values cannot explain the influence of the cross-linking process.

In Table I we have given the experimental values[1] of T_g obtained with samples of linear "anionic" polystyrene of low polydispersity $(\overline{M_w/M_n} \sim 1.1)$. We have calculated the values of ϵ, in accordance with eq 5, using the value $v_1 = 0.022$.

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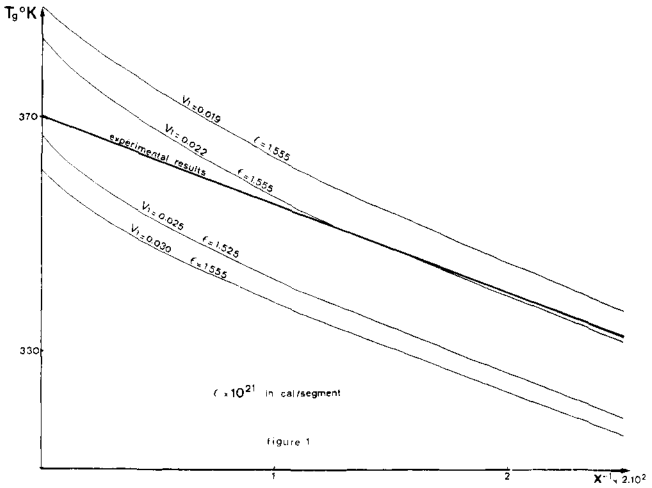

Figure 1. Variation of T_g against x^{-1}, making use of varying values of v_1, ϵ, and the experimental data of linear polymer chains.

Table I
Experimental Values of T_g[1] Obtained with Samples of Linear "Anionic" Polystyrene of Low Polydispersity ($\overline{M_n}/\overline{M_n} \sim 1.1$)[a]

$\overline{M_n}$	T_g, K	x	$\epsilon\times10^{21}$, cal/segment
7 500	350.7	144.2	1.584
10 450	356.0	201.	1.576
19 100	363.0	367.3	1.565
19 900	365.0	382.7	1.571
30 000	366.5	576.9	1.559
45 600	367.5	865.4	1.550
75 000	368.5	1442.3	1.540
1 100 000	370.4	21153.8	1.531

[a] The values of ϵ are calculated in accordance with eq 1 and with $v_1 = 0.022$.

The values calculated in this way were slightly higher than those of Gibbs,[11] which can mainly be explained by the difference in experimental results. However, in accordance with Spark,[12] ϵ is not a constant as the theory states and increases obviously with the chain ends fraction (M_n^{-1}).

III. Cross-Linked Polymers

The case of cross-linked polymers seems to be considerably more complex, by reason of the diversity of their topology and the variety of experimental conditions.

In 1964, Di Marzio[6] set forth a statistical theory based on Flory's lattice model, bringing into the entropic balance of the molecular model the influence of cross-linking. This calculation takes into account the loss entropy induced by the fact that each end chain is tied to a cross-link and is free to move around an average position equal to the mean square root end-to-end distance in the reference state (statistic of James and Guth[13]).

However, this description does not take into account the influence of the structural parameters of the network, in particular that of the functionality of the cross-links (between 3 and 4 for radical gels and cross-linked rubber, but varying for anionic gels[1]). This study resolves the problem of entropic contribution linked to the cross-linking process (the maintaining of chain ends at the mean-square end-to-end distance in the reference state), which is of essentially intermolecular origin.

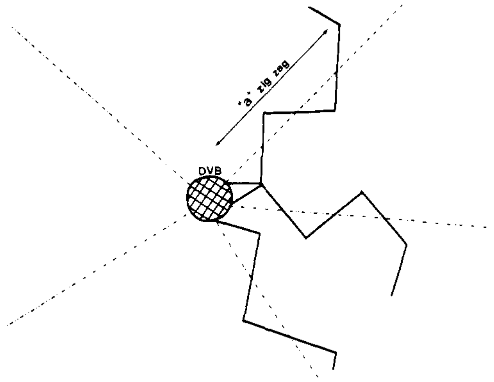

Figure 2. Intermolecular interactions around the cross-linked DVB nodules for a = 4.

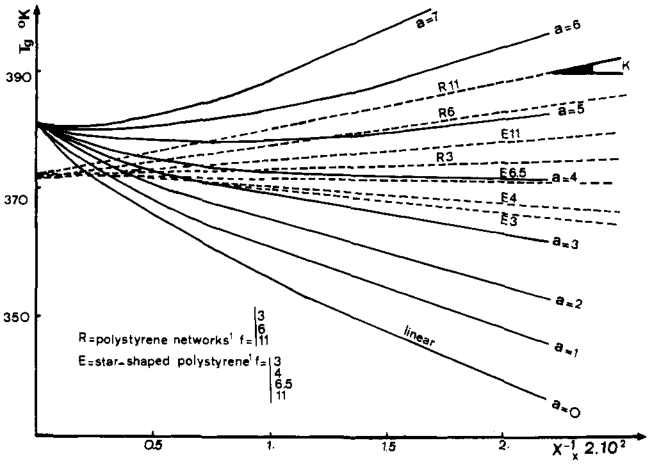

Figure 3. Variation of T_g against x^{-1} for different values of a according to eq 2 and experimental results for cross-linked and star-shaped polymers of varying functionality.[1]

Table II.
Experimentally Determined T_g Values for Star-Shapped and Cross-Linked Polymers[1] and the Corresponding Slopes, K, for the $T_g = f(\overline{M_n}^{-1})$ Representation.

Star-shaped polymers				Cross-linked polymers			
f	$\overline{M_n}$/ branched	T_g, °C	K_{measured} × 10^{-5}	f	$\overline{M_n}$/ branched	T_g, °C	K_{measured} × 10^{-5}
3	10 880	93.5		3	9 600	98.5	
	23 200	95.5			12 100	98	+0.13
	50 450	96.3	−0.41		27.550	97.7	
	80 000	96.7		6	10 450	103	
	319 000	97.1			10 660	102.5	
4	16 670	96.2			13 200	101.7	
	61 900	96.9			19 900	100.7	+0.55
	134 300	97.1	−0.27		30 000	99.0	
	200 000	97.5			45 600	98.6	
	480 000	97.6			75 000	97.7	
6.5	35 200	98.1		11	8 000	109.5	
	52 270	97.7			20 000	103.5	+0.78
	100 000	97.9	+0.1		36 000	102.0	
	518 200	98.7					
11	53 360	98.2					
	54 540	98.1	0.26				
	172 700	97.8					

Di Marzio's theory, however, is based on a monomeric model in which the linking order of polymeric segments is of little importance given the low value of the free volume fraction present at $T = T_g$. It follows, in this case, that the influence of intermolecular interactions, caused by the cross-linking process, is doubtless not negligible when compared to the intermolecular entropic contribution. In the case of networks prepared by anionic polymerization, this influence is localized all around the cross-linked nodules, whereas that of physical entanglements is certainly negligible[1] (Figure 2). On the other hand, the situtation is reversed in the case of radical networks in which the effect of concentration causes a considerable amount of physical entanglements.

We have modified Gibbs and Di Marzio's theory, supposing that, among the $(1 - f)N_2(x - 2)$ zig-zags which are present, a supplementary zig-zags are disposed near to the cross-linking nodules. Their presence, as we have already stated, is imposed by a volume effect among different chains of the same nodule, which depends on the functionality and size of the nodule (Figure 2).

The relation in eq 5 becomes:

$$\frac{1}{x-2-a}\left|\frac{v_1}{xv_2}\log v_1 - \log 2x + x - 1\right| = \frac{2e^{-\epsilon/RT_g}}{1+2e^{-\epsilon/RT_g}}\frac{\epsilon}{RT_g} + \log\left(1 + 2e^{-\epsilon/RT_g}\right) \quad (6)$$

We have plotted in Figure 3 the variation of T_g against x^{-1} for different values of a according to eq 6. For a given molecular weight $\overline{M}_n$, the cross-linking effect makes the T_g value from the base line $a = 0$ (linear polymer) to the cluster of straight lines $a = 4, 5, 6$ in proportion to the value of the average functionality of the cross-linked nodules. The experimental results corresponding to the dotted lines on Figure 3 are given in Table II. This result reveals clearly the volume effect induced by the cross-links whose influence is very important, as all of the experimental results can be approximately situated between the values $a = 4$ and 6.

These results show that the effect of intermolecular interaction caused by cross-linking can explain quite adequately all of the thermomechanical properties of cross-links of different functionality.

However for a given functionality, the cross-linked networks show a much higher slope than that of star-shaped polymers. This result can be easily explained as in the first case if the chain contains a supplementary zig-zigs at the two chain extremities and in the second case if there are only $a/2$ supplementary zig-zags at the one cross-linked chain extremity. We can then see that the volume effect near the cross-links seems to be less important for the networks than for star-shaped polymers, while the a values are not very different, for a given functionality. This effect can be explained if we consider that star-shaped polymer chains have a much more super-coiled conformation that cross-linked chains and that is why the segment density is higher in the vicinity of this nodule.[1]

References and Notes

(1) F. Rietsch, D. Daveloose, and D. Froelich, *Polymer*, **17**, 859 (1976).
(2) D. J. Worsfold, J. G. Zilliox, and P. Rempp, *Can. J. Chem.*, **47**, 3379 (1969).
(3) P. Weiss, G. Hild, J. Herz, and P. Rempp, *Makromol. Chem.*, **135**, 249 (1970).
(4) J. H. Gibbs and E. A. Di Marzio, *J. Chem. Phys.*, **28**, 373 (1958).
(5) E. A. Di Marzio and J. H. Gibbs, *J. Polym. Sci., Part A-1*, 1417 (1963).
(6) E. A. Di Marzio, *J. Res. Natl. Bur. Stand., Sect. A*, **68**, 611 (1964).
(7) E. A. Di Marzio and J. H. Gibbs, *J. Polym. Sci.*, **40**, 121 (1959).
(8) J. Moacanin and R. Simha, *J. Chem. Phys.*, **45**, 964 (1966).
(9) T. G. Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955).
(10) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
(11) J. H. Gibbs, *J. Chem. Phys.*, **25**, 185 (1956).
(12) K. Onder, R. H. Peters, and L. C. Spark, *Polymer*, **13**, 133 (1972).
(13) H. M. James and E. Guth, *J. Chem. Phys.*, **11**, 455 (1943).

Biphenylene as a Cross-Linking Site in Thermally Stable Polymers

A. Recca and J. K. Stille*

Department of Chemistry, Colorado State University,
Fort Collins, Colorado 80523. *Received October 18, 1977*

ABSTRACT: Thermally stable aromatic polymers have been cross-linked by employing the thermal cleavage reaction of biphenylene units incorporated into the polymer chain. Polyamides were synthesized by substituting biphenylene-2,6-dicarboxylic acid chloride for isophthaloylchloride in polymerizations with two different amines. A polybenzimidazole was prepared by substituting dimethyl diphenylene-2,6-dicarboxylate for dimethyl terephthalate in a polymerization with 3,3′,4,4′-tetraaminodiphenyl ether tetrahydrochloride. Polyquinoxalines were synthesized by substituting 2,6-diglyoxalyldiphenylene for dibenzyl derivatives in polymerizations with 3,3′,4,4′-tetraaminodiphenyl ether. The cured polymers showed an increase or disappearance of T_g, complete insolubility, and higher moduli particularly above the T_g.

The introduction of biphenylene in aromatic polyquinolines[1-3] and polyether ketones[4] affords an attractive cross-linking mode because no volatile materials are produced during the cross-linking reaction and the resulting cross-links are thermally stable.

In this study we have investigated the cross-linking reaction of several thermally stable polymers such as polyamides, polybenzimidazoles, and polyquinoxalines containing small amounts of biphenylene in the chain.

Results and Discussion

Monomers. Biphenylene (**1**) and 2,6-diacetylbiphenylene (**2**) were prepared following the procedure described elsewhere[2,5,6] (Scheme I). Biphenylene-2,6-dicarboxylic acid (**3**) was obtained by oxidation of 2,6-diacetylbiphenylene (**2**) with commercial sodium hypochlorite solution. The product was obtained in high yield (89%) when the reaction was carried out at relatively low temperature (40 °C) for 24 h in the presence of tetrabutylammonium hydroxide as a phase-transfer catalyst. Under these conditions, the reaction was complete after 4 h.

The diacid was easily converted with thionyl chloride to biphenylene-2,6-dicarboxylic acid chloride (**4**) which was esterified with methanol to obtain the dimethyl diphenylene-2,6-dicarboxylate (**5**). The selenium dioxide oxidation of 2,6-diacetylbiphenylene (**2**) gave 2,6-diglyoxalyldiphenylene dihydrate (**6**) in 43% yield.

0024-9297/78/2211-0479$01.00/0