Macromolecules **1980**, *13*, 1568-1571

Flex Volumes and Flex Energies in Liquid Poly(vinyl acetate)

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ABSTRACT: Volumes and energies associated with the flexing (i.e., rotational isomerization) of main-chain bonds in liquid poly(vinyl acetate) have been calculated and compared with changes in volume and internal energy of the liquid. For this polymer with a three-state rotational model including the "pentane interference" the flex contribution to ΔC_p and to the increase in thermal expansivity ($V\Delta\alpha$) in the glass-liquid transition is 20%. For amorphous polyethylene, which has no articulate substituent, both of these contributions are estimated to be ~40%. The results for the two polymers suggest a new relationship at the glass transition: $\Delta C_p / V\Delta\alpha = (\mathrm{d}\ln T_0/\mathrm{d}p)^{-1}$, where T_0 is the parameter in the Vogel equation for polymer liquid mobility.

Introduction

In earlier papers[1,2] it was shown that for a three-state rotational isomeric model (a trans state t and two equivalent gauche states, g^+ and g^-) the energy difference is given by

$$U = mRT_0 \tag{1}$$

in which T_0 is the constant in the Vogel equation for polymer liquid mobility and is the temperature at which the conformational entropy S_c *appears* to extrapolate to zero. For independent bond rotations[1] $m = 4.2$ in eq 1 but if transitions between *gauche* states of opposite sign are excluded (the "pentane interference"), $m = 4.0$ or 4.4, depending upon which of two rotational partition functions is chosen.[2]

The U values derived from eq 1 for a polymer liquid are found to be significantly higher than U^* generally attributed to the "isolated" or "unperturbed" chain and it was suggested[1,2] that this difference is due to an intermolecular perturbation on U^* which is manifested by the pressure dependence of T_0. The physical basis for this intermolecular effect is that the flexing of main-chain bonds from the trans state to the g^+, g^- states involves a disordering and hence an intrinsic increase in volume which in itself can contribute to the internal energy E of the liquid.

A derivation of this flex (i.e., conformational) volume was reported[2] for linear polyethylene (PE) at atmospheric pressure, P_0. The present paper pursues this concept for liquid poly(vinyl acetate) (PVAc) on which there is already a considerable amount of data on equilibrium properties over a broad range of P-V-T conditions down to the glass transition.[3-5] Detailed results will be given only for the three-state model with "pentane interference", using the simpler of the two rotational partition functions:[2] $Q = 1 + 2^{1/2}\exp(-U/RT)$ ($m = 4.0$ in eq 1). Parallel calculations were made also for independent rotations[1] ($Q = 1 + 2\exp(-U/RT)$ and $m = 4.2$) and this will be designated as the *alternate* model. The major conclusions turn out to be the same for both cases.

General Equations[1,2]

$$Q = 1 + 2^{1/2}\exp(-U/RT) \tag{2}$$

$$S_c = R\ln Q + (U/T)(Q-1)/Q \tag{3}$$

$$C_{pc} = R(U/RT)^2(Q-1)/Q^2 \tag{4}$$

$$(\partial\nu/\partial T)_p = -(\partial S_c/\partial p)_T = C_{pc}(\partial\ln U/\partial p)_T \tag{5}$$

In eq 5, ν is the flex volume and $(\partial\ln U/\partial p)_T = \mathrm{d}\ln T_0/\mathrm{d}p$. The fraction of flexed (g^+, g^-) bonds is given by

$$f = (Q-1)/Q \tag{6}$$

and the flex energy is

$$E_c = fU \tag{7}$$

Table I
Molar Flex Volumes for PVAc

P, bars	ΔT_0,[a] deg	$10^2\mathrm{d}T_0/\mathrm{d}p$, deg/bar	V_c, cm³/mol
0	0	1.757	5.843
200	3.25	1.502	4.996
400	5.99	1.278	4.250
600	8.32	1.084	3.606
800	10.35	0.921	3.063
1000	12.09	0.788	2.622

[a] T_0 (K) = 248 + ΔT_0, U (cal/mol) = $4.0RT_0$, U = 1971 cal/mol at P_0.

Results

1. Flex Volumes. The earlier[2] derivation of the molar flex volume V_c involved the differentiation of eq 3, leading to eq 4 and 5, followed by reintegration of eq 5. The observed[2] linear relationship between the fraction of flexed bonds f and the actual flex volume ν at constant pressure suggests a more direct procedure as follows:

$$\nu = fV_c \tag{8a}$$

$$(\partial\nu/\partial T)_p = (\partial f/\partial T)_p V_c \tag{8b}$$

But from eq 6

$$\begin{aligned}(\partial f/\partial T)_p &= (U/RT^2)(Q-1)/Q^2 \\ &= C_{pc}/U\end{aligned} \tag{8c}$$

Combining eq 8b and 8c with eq 5 eliminates C_{pc} and gives the simple relationship

$$V_c = \mathrm{d}U/\mathrm{d}p = mR(\mathrm{d}T_0/\mathrm{d}p) \tag{9}$$

the latter term arising from eq 1. In eq 9, $R = 83.14$ (cm³ bars)/(mol deg) and for the model we are using, $m = 4.0$.

The pressure dependence of T_0 has been expressed by a cubic equation[6] whose pressure derivative is

$$\mathrm{d}T_0/\mathrm{d}p = a_1 + 2a_2P + 3a_3P^2 \tag{10}$$

in which for PVAc the coefficients are $10^2a_1 = 1.757$, $10^6a_2 = -6.753$, and $10^9a_3 = 1.273$. Table I lists the molar flex volumes V_c computed by eq 10 and 9 for 200-bar increments up to 1000 bars.

It is of interest to compare V_c for PVAc at atmospheric pressure (P_0) with the corresponding values for polystyrene (PS) and linear polyethylene (PE). For these two polymers $10^2(\mathrm{d}T_0/\mathrm{d}p) = 2.487$ and 1.303 deg/bar, respectively,[7] and by eq 9, $V_c = 8.27$ and 4.33 cm³/mol, the latter value agreeing with that derived previously[2] for PE by the longer procedure. The van der Waals volumes are[8,9] V_w (cm³/mol) = 22.94 (PVAc), 31.42 (PS), and 10.23 (PE), giving the ratios $V_c/V_w = 0.255$, 0.263, and 0.423, respectively. The much lower ratios for PVAc and PS are explained by noting that the side substituents in these two polymers contribute to V_w but not to V_c since the latter involves only the volume increment due to flexing of *main-chain* bonds.

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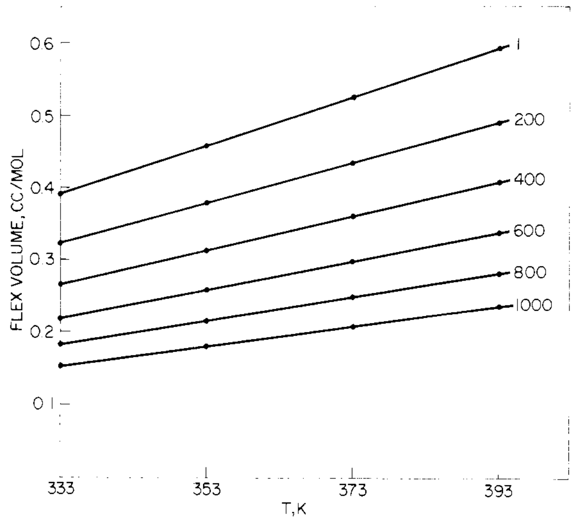

Figure 1. Flex volumes in PVAc liquid as functions of temperature and indicated pressures (bars).

Table II
Energies and Volumes for PVAc at P_0

T, K	304 (T_g)	323	343
C_p,[a] cal/(mol deg)	18.48	18.89	19.32
ΔE,[a] cal/mol	0	367	749
ΔV,[a] cm^3/mol	0	0.506	1.038
f	0.0513	0.0615	0.0727
E_c, cal/mol	101.2	121.3	143.3
ν, cm^3/mol	0.300	0.359_5	0.425
$\Delta E/\Delta E_c$		18.4	17.8
$\Delta V/\Delta \nu$		8.5	8.3

[a] 1 mol = 43 g.

Similar effects will be observed later at the glass transition.

Figure 1 displays the ν–T isobars calculated from eq 8a up to 1000 bars. These are linear,[10] with the slopes decreasing with increasing pressure and resembling the behavior of polymer liquid specific volumes. At P_0, $10^3 \cdot (\partial \nu/\partial T)_p = 3.38$ cm^3/(mol deg). The *alternate* model also gives linear isobars but with slightly increased ν values and with steeper slopes. At P_0, for example, $10^3(\partial \nu/\partial T)_p = 4.42$ cm^3/(mol deg), about 31% higher than the value above.

By combining eq 7 and 8a we have

$$E_c/\nu = U/V_c \tag{11}$$

which should apply to any P–V–T state of the liquid. Since the molar quantities U and V_c are constant at constant pressure, the E_c/ν ratio will likewise remain constant under these conditions. Also, from eq 1 and 9

$$U/V_c = (\mathrm{d} \ln T_0/\mathrm{d}p)^{-1} \tag{12}$$

leading to the interesting conclusion that the U/V_c and E_c/ν ratios are independent of the rotational model since m cancels out.

2. Energies and Volumes at Constant Pressure. The change in internal energy E with temperature at constant pressure is given by the thermodynamic relation

$$(\partial E/\partial T)_p = C_p - P(\partial V/\partial T)_p$$

in which for atmospheric pressure the last term is negligible compared to C_p. Using the mean of the equations for C_p(liquid) reported by McKinney and Simha[5] "near T_g" and by Sasabe and Moynihan[11] (300–340 K) we have

$$C_p \text{ (cal/(mol deg))} = 11.91 + 0.0216T$$

and by integration

$$\Delta E \text{ (cal/mol)} = 11.91(T_2 - T_1) + 0.0108(T_2^2 - T_1^2)$$

Table III
Effects of Pressure on Flex Properties of PVAc Liquid at 353 K

P, bars	$10^2 f$	ν, cm^3/mol	E_c, cal/mol
0	7.84	0.458	154.6
200	7.58	0.379	151.4
400	7.37	0.313	148.7
600	7.19	0.259	146.4
800	7.04	0.216	144.5
1000	6.91	0.181	142.8

Table IV
Internal Pressures for PVAc at 353 K

P, bars	$10^5\beta$, bar^{-1}	$10^4\alpha$, deg^{-1}	γ, bar/deg	$(\partial E/\partial V)_T$,[a] cal/cm^3
0	6.17	7.22	11.70	98.68
200	5.49	6.75	12.30	99.01
400	4.94	6.37	12.89	99.18
600	4.50	6.07	13.47	99.29
800	4.14	5.81	14.03	99.23
1000	3.83	5.59	14.58	99.13

[a] $P_i = (\partial E/\partial V)_T = T\gamma - P$, where $\gamma = \alpha/\beta$.

Table V
Effects of Pressure on Energy and Volume Ratios at 353 K

P, bars	$-\Delta V$,[a] cm^3/mol	$-\Delta E$,[a] cal/mol	$\Delta E/\Delta E_c$	$\Delta V/\Delta \nu$
0	0	0		
200	0.430	42.5	13.3	5.4
400	0.813	80.4	13.6	5.6
600	1.161	115.0	14.0	5.8
800	1.483	147.0	14.6	6.1
1000	1.763	174.7	14.8	6.4

[a] 1 mol = 43 g.

The results are listed in the upper part of Table II, with $T_1 = T_g = 304$ K as the reference temperature. The ΔV values are derived directly from ref 3 (Table 1). The lower part of Table II gives the flex energies and flex volumes computed by eq 6, 7, and 8a. The ratios $\Delta E/\Delta E_c$ and $\Delta V/\Delta \nu$ change very slightly (2–3%) with temperature.[12]

3. Energies and Volumes at Constant Temperature. The effects of isothermal compression at 353 K (80 °C) on the flex properties are shown in Table III. Between P_0 and 1000 bars f and E_c decrease by 12% and 7.6%, respectively, and by far the greatest decrease (60%) is in ν, largely because of the strong dependence of the molar flex volume V_c on pressure (Table I). The E_c/ν ratio changes from 337 cal/cm^3 at P_0 to 788 cal/cm^3 at 1000 bars.

For a comparison of these values with the changes in the liquid volume and internal energy the "internal pressure" P_i as a function of applied pressure was calculated (Table IV). The procedure for computing the pressure dependence of the thermal pressure coefficient γ via the Tait equation has been described previously.[2] The Tait constants ($c = 0.0894$ and $b = 1448$ bars at 353 K) and the thermal expansion coefficient at P_0 are from the work of McKinney and Simha.[4] Specific volumes involved in this calculation were taken directly from Table 1 of ref 3, while the value at 1000 bars was derived through the Tait equation. The change in internal energy ΔE, with P_0 as the reference pressure, was then estimated by a stepwise summation: $\Delta E = \sum \bar{P}_i \Delta V$, where $\bar{P}_i$ is the mean value for each 200-bar interval and ΔV is the volume change over the same interval (Table V). The values for ΔE agree with those calculated by eq 4 of ref 5, which is explicit in ΔE in terms of the Tait constants. In the last two columns of Table V, ΔE and ΔV are compared with ΔE_c and $\Delta \nu$

Table VI
Comparisons of Flex Contributions at T_g

	PE[a]	PVAc
$(\partial \nu/\partial T)_p/V\Delta\alpha$	0.42	0.195
$(\partial \nu/\partial T)_p/(\partial V/\partial T)_p$	0.305	0.118
$C_{pc}/\Delta C_p$	0.38	0.20
C_{pc}/C_p (liquid)	0.158	0.056
$\Delta E_c/\Delta E$ (liquid)[b]	0.164	0.054

[a] From Appendix. [b] T_g to T_g + 40 K.

derived from Table III. The $\Delta E/\Delta E_c$ ratio increases by only 11% between P_0 and 1000 bars while the $\Delta V/\Delta\nu$ ratio shows a larger increase (18%), the latter again reflecting the greater sensitivity of ν to pressure, as mentioned earlier.

4. Flex Contributions at the Glass Transition. From Table 9b of ref 3, $10^3 V\Delta\alpha = 0.3643$ cm^3/(g deg) = 15.67 cm^3/(mol deg) at T_g = 304 K. By eq 8b and 8c we find $10^3(\partial\nu/\partial T)_p$ = 3.058 cm^3/(mol deg) and hence, $(\partial\nu/\partial T)_p/V\Delta\alpha = 0.195$.

McKinney and Simha[5] found ΔC_p = 0.50 J/(g K) = 5.14 cal/(mol deg) at T_g, agreeing with independent measurements by Sasabe and Moynihan[11] on the same sample. The conformational (i.e., flex) heat capacity calculated by eq 4 is C_{pc} = 1.032 cal/(mol deg), giving $C_{pc}/\Delta C_p = 0.20$. The agreement with the ratio of the thermal expansibilities above does not necessarily confirm our absolute values for $(\partial\nu/\partial T)_p$ and C_{pc} since by eq 5 the former is directly proportional to the latter. Rather, this agreement tends to confirm our derived value for d ln U/dp = d ln T_0/dp at P_0. From Table II, C_p(liquid) = 18.28 cal/(mol deg) at T_g and thus C_{pc}/C_p(liquid) = 0.056, agreeing with $\Delta E_c/\Delta E$ = 0.054 in the vicinity of T_g, as it should. For constant volume at T_g, ΔC_v = 0.31 J/(g K) = 3.184 cal/(mol deg),[5] which, with our value of C_{pc}, does not support the concept[13,14] that $\Delta C_v = C_{pc}$ and agrees with the conclusion by Roe and Tonelli.[15]

For the *alternate* rotational model the respective ratios at T_g are $(\partial\nu/\partial T)_p/V\Delta\alpha = 0.25$ and $C_{pc}/\Delta C_p = 0.26$, both about 30% higher than for the model which includes the "pentane interference".

Discussion

The $\Delta E/\Delta E_c$ ratios found in this work suggest a relatively constant contribution by the main-chain flex energy E_c to the total internal energy E in liquid PVAc. In the isothermal compression (Table V) the seemingly small change in U with pressure, $\Delta U = 4.0R\Delta T_0$ (Table I), is sufficient to maintain a virtually constant $\Delta E/\Delta E_c$ ratio despite the large changes in E and E_c themselves. The conformational (i.e., flex) contributions by the main chain to total energy and volume of the liquid have been separated from the contributions by the acetate substituent. To emphasize this point the various ratios for PVAc at T_g are compared in Table VI with those for PE (Appendix), which has no "articulate" substituent. The symmetry between PE and PVAc should be noted. With respect to both ΔC_p and $V\Delta\alpha$ the flex contribution in PE is twice that in PVAc. With respect to C_p and $(\mathrm{d}V/\partial T)_p$ for the liquid at T_g, the flex contribution in PE is 2.6–2.8 times that in PVAc. All of these values are consistent with the explanation given earlier for the respective V_c/V_w ratios.

The observation that $C_{pc}/\Delta C_p \simeq (\partial\nu/\partial T)_p/V\Delta\alpha$ for both PVAc and PE at T_g is especially significant. Rearranging and applying eq 5 we obtain

$$\Delta C_p/V\Delta\alpha = C_{pc}/(\partial\nu/\partial T)_p = (\mathrm{d}\ \ln T_0/\mathrm{d}p)^{-1} \quad (13)$$

Boyer[23] has suggested cross comparisons of ΔC_p and $V\Delta\alpha$ as a means of assessing the relative merits of conflicting sets of data and in his Figure 3 shows a broad correlation of the $\Delta C_p/V\Delta\alpha$ ratio for a variety of polymers. It may be noted that for partially crystalline polymers ΔC_p and $V\Delta\alpha$ individually will depend upon the degree of crystallinity but this should cancel out in the $\Delta C_p/V\Delta\alpha$ ratio for the same degree of crystallinity.[23] According to eq 13, this ratio should equal (d ln T_0/dP)$^{-1}$, which can be derived independently from the Vogel T_0 and its initial-pressure coefficient. This relationship should be examined for other polymers.

Acknowledgment. Helpful comments by R. Simha and A. E. Tonelli as reviewers were appreciated. We thank the National Science Foundation for support under Grant No. DMR 76-20090 (Polymers Program).

Appendix

In linear polyethylene (PE) crystallinity has precluded direct measurements of either ΔC_p or $\Delta\alpha$ at T_g, which we take to be 200 K for the completely amorphous polymer.[1,2,16] However, by extrapolation from the lower n-alkanes Broadhurst[17] has calculated ΔC_p = 2.78 cal/(mol deg) as the difference between the liquid and the crystalline solid at 200 K. With the reasonable assumption that C_p(glass) $\simeq$ C_p(crystal) the above value should also represent ΔC_p for the glass–liquid transition.[18] By eq 1, 2, and 4 with T_0 = 160 K[1,2,16] we obtain C_{pc} = 1.048 cal/(mol deg) and $C_{pc}/\Delta C_p$ = 0.38. Similarly,[17] C_p(liquid) = 6.636 cal/(mol deg) at 200 K and thus C_{pc}/C_p(liquid) = 0.158. For the temperature interval T_g to T_g + 40 K in the liquid,[17] $\Delta E = \Delta H$ = 272 cal/mol. By eq 1, 2, and 7 we obtain ΔE_c = 44.5 cal/mol for the same temperature range and hence $\Delta E_c/\Delta E$ = 0.164, agreeing with the ratio of the heat capacities, as it should.

By extrapolation from the lower n-alkanes we derived[19] V = 1.080 cm^3/g for the specific volume of PE liquid at 200 K. Invoking the Simha–Boyer rule[20] ($\Delta\alpha T_g$ = 0.113), we obtain $10^3 V\Delta\alpha$ = 8.54 cm^3/(mol deg). By eq 8a and 8b with V_c = 4.33 cm^3/mol (cf. section 1), $10^3(\partial\nu/\partial T)_p$ = 3.57 cm^3/(mol deg) and thus $(\partial\nu/\partial T)_p/V\Delta\alpha$ = 0.42 at 200 K, in satisfactory agreement with the $C_{pc}/\Delta C_p$ ratio. Olabisi and Simha[21] reported an exponential V–T equation for liquid PE which by extrapolation[22] gives $10^4(\partial V/\partial T)_p$ = 8.37 cm^3/(g deg) at 200 K and hence for the liquid at T_g, $(\partial\nu/\partial T)_p/(\partial V/\partial T)_p$ = 0.305.

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Rubber Networks Containing Unattached Macromolecules. 5. Stress Relaxation in Styrene–Butadiene–Styrene Block Copolymer with Unattached Linear and Star Polybutadienes[1]

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Received May 21, 1980

ABSTRACT: Stress relaxation has been studied in networks of styrene–butadiene–styrene block copolymer with spherical styrene domain structure containing 0.10 weight fraction of unattached linear or star-branched polybutadiene with the same microstructure as the butadiene block. Stress relaxation measurements were also made on networks containing no unattached species and containing the same weight fraction of hydrocarbon oil and on one of the linear polybutadienes. Equivalent viscoelastic data for the other uncross-linked polybutadienes were obtained from measurements of dynamic storage and loss moduli by Graessley and creep by Plazek. The stretch ratio was usually 1.15 and the temperature range from −20 to +20 °C. The Young's relaxation modulus was calculated from the neo-Hookean stress–strain relation. For the uncross-linked linear polymers (M_w = 203 000, 389 000, and 813 000), the time dependence of the relaxation modulus agreed rather well with the Doi–Edwards theory as modified for a slight degree of molecular weight distribution, and the disengagement time was proportional to the third power of the molecular weight. For the star-branched uncross-linked polymers (3-arm, M_w = 204 000; 4-arm, 88 000 and 226 000), the relaxation was much more gradual but eventually reached low modulus values. The contribution of the unattached species in the network to the relaxation modulus, $E_1(t)$, was calculated by difference; after multiplication by $(1 - v_2'^{2})^{-1}$, where v_2' is the volume fraction of polybutadiene block in the continuous polybutadiene phase, it was compared with the relaxation modulus measured directly for the uncross-linked polymer, $E_{11}(t)$, for each unattached species. For the linear polymers, the relaxation was slower in the network than in the environment of the linear species alone by about half an order of magnitude, but the form of the time dependence was the same. For the star-branched polymers, the relaxation was very much slower in the network. It may be concluded that the suppression of reptation by branching is much more effective when the topological obstacles are trapped entanglements on strands with anchored ends than when they are untrapped entanglements on strands with free ends.

In previous papers in this series,[3-6] viscoelastic properties have been reported for conventionally cross-linked[3-5] and end-linked[6] networks containing unattached linear macromolecules, whose relaxation can be attributed to reptation[7] or contour diffusion processes.[8,9] A question of particular interest has been the influence of branching on reptation. It is well-known that long-chain branching with sufficiently long branches increases the viscosity of an uncross-linked polymer enormously and prolongs the relaxation times in the terminal zone.[10] Specifically, de Gennes has pointed out that long-chain branching should essentially eliminate the reptation mechanism for relaxation.[11] We have undertaken a comparison of relaxation of linear and star-branched molecules in still another type of network, namely, that formed by domain separation in a poly(styrene–butadiene–styrene) triblock copolymer (SBS). The unattached molecule is a polybutadiene whose microstructure matches that of the butadiene block to ensure compatibility. Viscoelastic properties of blends of this type with linear unattached molecules have been examined previously by Toy, Niinomi, and Shen[12] and Kraus and Rollmann.[13] In the latter study (in which a (SB)$_n$ multiblock copolymer was used), the frequency location of the viscoelastic loss associated with relaxation of the unattached species, as judged by either the loss tangent maximum or the loss modulus maximum, was found to be approximately inversely proportional to the third power of the molecular weight, as predicted for the reptation mechanism.[7-10] In our experiments, three linear and three star-branched polybutadienes have been studied and their contributions to stress relaxation in a triblock copolymer network have been compared with the relaxations of the respective uncross-linked polymers themselves. The volume fraction of the unattached species in the polybutadiene phases of the SBS network was 0.15. Thus we compare motions of the same molecule in its own loose entanglement network and in a network whose entangled strands are anchored by polystyrene domains. The essential difference between the two media in which the unattached molecules are relaxing is that the entanglements of the surrounding molecules are untrapped and trapped, respectively. However, the steric effects of the polystyrene domains may also influence the mobility of the unattached species.

Experimental Section

The SBS block polymer and one linear (389L), one 3-arm star (204S3), and one 4-arm star (226S4) polybutadiene were synthesized at The University of Akron. The synthesis followed procedures outlined elsewhere.[14-16] *sec*-Butyllithium was used as the initiator with benzene as the polymerization solvent. All reactions were carried out at about 30 °C. Methyltrichlorosilane and silicon tetrachloride were used as the linking agents for the formation of the 3- and 4-arm polybutadiene stars.

The GPC analysis of these near-monodisperse polymers was carried out by using a seven-column Styragel set with tetrahydrofuran as the carrier solvent. The characteristics of this

0024-9297/80/2213-1571$01.00/0