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Correlation of Liquid-State Compressibility and Bulk Modulus with Cross-Sectional Area per Polymer Chain

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ABSTRACT: Liquid-state compressibilities, $\kappa = -(1/V_0)(\partial V/\partial P)$, determined at $P \to 0$ and at the liquid–liquid transition (relaxation), $T_{ll} \sim 1.2T_g$ (K), increase as $A^{0.54}$, where A is the cross-sectional area per polymer chain calculated at 20 °C from X-ray lattice parameters. κ increases from 3.8×10^{-5} to 7.4×10^{-5} bar^{-1} as A increases from 0.280 to 0.934 nm^2. Since $A^{0.5}$ is an average interchain distance, κ thus increases linearly the further apart are the chains. The bulk modulus, $\bar{K}$, and the Tait equation parameter, b, both in bars, decrease as $A^{-0.52}$, again at $P \to 0$ and at T_{ll}. Correlations of κ, $\bar{K}$, and b with A at T_g + 100 K were inferior to those at T_{ll}, with smaller correlation coefficients and larger standard errors. T_{ll} thus appears to be a useful liquid-state reference temperature. Corrections for thermal expansion and ratios of amorphous density to crystalline density were not made. κ values for linear and branched PE's and for a mixed-isomer PBD did not fit the correlation, with κ being high. Values of κ for the glassy state at $T \to T_g$ did not correlate with A. Ability to detect liquid-state transitions from isothermal V–P data should increase with area per chain because of enhanced compressibility. This is demonstrated for PS.

Introduction

We have been interested for some time in empirical or semiempirical correlations of selected physical properties of polymers with cross-sectional area, A, of polymer chains. Properties studied thus far are the Mooney–Rivlin C_2 constant,[1,2] the chain entanglement parameter N_c,[3,4] surface fold energy σ_e,[5] the chain stiffness parameter σ,[6] and the critical tensile strength.[7]

Areas are calculated from X-ray lattice parameters of crystalline polymers or by several indirect methods for amorphous polymers and copolymers.[2,4] In addition to values of A that have been published,[2,4] one of us maintains an extensive tabulation of A values.[8] As explained earlier,[2] values of A are valid at 20 °C and are assumed to hold for amorphous polymers even though derived for crystalline polymers. We justified this practice since the ratio of amorphous density to crystalline density is about 0.9 for many polymers.[2] Also, we do not correct herein for effects of thermal expansion on A.

We have examined correlations of still other polymer properties with A. These are as yet not formalized into a finished product. In the course of such studies we became aware that the liquid-state isothermal compressibility, κ, increases with area, where κ at $P \to 0$ is defined as

$$\kappa = -(1/V_0)(\partial V/\partial P) \tag{1}$$

with V being the specific volume in cm^3 g^{-1} at the pressure in bars (P) and V_0 the specific volume at zero pressure, giving κ the dimension of bars^{-1}. κ is a function of both T and P. It increases with T and decreases with P at constant T. Both of these facts complicated our early attempts at correlation of κ with A. We arbitrarily chose values of κ at T_g + 100 °C and P = 1 bar in our original correlations but this choice for a reference temperature was not satisfactory. κ did increase with log A but there was considerable scatter.

The problem is analogous to that with the monomeric friction coefficient, Ξ_0, calculated from melt viscosity data. Ξ_0 is also a function of T. Ferry[9] has presented tabulated values of Ξ_0 at several different temperatures, i.e., 298 K, T_g + 100 K, etc.

Procedural Details

We have elected in what follows to calculate κ at T (K) = kT_g (K), where k is a constant slightly greater than unity. The evolution of this choice is as follows.

κ is commonly obtained from isothermal V–P data as eq 1 suggests. One of us has been analyzing published V–P data[10–13] and isobaric V–T data at $P \leq 600$ bar,[14] as a means of locating secondary liquid-state transition (relaxation) temperatures, notably the liquid–liquid events designated by us as T_{ll} and T_{ll}'.[15–17] (See Appendix for terminology.) Pertinent to the present study was the determination of the Tait equation parameter, b, in bars, as a function of temperature.[12] Specifically, we calculated b as $P \to 0$ and labeled this value as b^*.

We have discussed elsewhere[10] the approximate relationship

$$\kappa \cong (C/b)(1 - P/b) \tag{2}$$

valid for $P/b < 0.4$. C is a constant, usually given as 0.0894 unless noted otherwise.[10] One obtains κ at $P \to 0$ as C/b^*. We showed[12] that b^* decreased linearly with T from $T_g < T < T_{ll}$ and again linearly with a smaller slope above T_{ll}. κ will therefore increase with T somewhat curvilinearly but with a distinct slope change at T_{ll}. It was proposed tentatively[12] that T_{ll} be considered a liquid-state reference temperature. Plots of b^* vs. T/T_{ll} for many of the polymers in Table I are shifted horizontally to coincide at T/T_{ll} = 1 but are separated vertically by structure. (See Figures 6 and 7 of ref 12.)

Slopes, $\mathrm{d}b^*/\mathrm{d}T$, below and above T_{ll}, given in Table III of ref 12, are different for each polymer. This study[12] convinced us that T_{ll} might be considered a reference temperature characteristic of the liquid state. Since T_{ll} (K)/T_g (K) $\sim 1.20 \pm 0.05$ for most polymers with $\bar{M}_n$ above the oligomeric range,[12–17] one may prefer to consider our

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Table I
Isothermal Compressibility, κ, at T_{ll} ($P \rightarrow 0$) and Cross-Sectional Area per Polymer Chain

polymer	area[a,b] per chain, nm^2	T_{ll}, °C	source of T_{ll}	κ at T_{ll}, units of 10^{-5} bar^{-1}	source of κ at T_{ll}
PCHMA	0.934	165	*c*	7.39	*d*
P*n*BMA	0.936	95	*c*	6.57	*d*
P*o*MS	0.903	170	*c*	7.33	*d*
PS	0.698	155	*c*	6.32, 6.88	*d*
iso-PMMA	0.638	110	*c*	5.18	*d*
a-PMMA	0.638	165	*c*	6.17	*d*
PVAc	0.593	70	*c*	6.02	*d*
PIB	0.412	-10	*e*	4.39	*f*
a-PP	0.342	-10	*f*	4.16	*f*
cis-PI	0.280	-30	*e*	3.85	*f*

[a] From ref 8 except for PCHMA, whose source is given in the discussion section. Values of A are determined at room temperature and not corrected for thermal expansion or ratio of amorphous density to crystalline density. A for a-PMMA is assumed to be the same as that for iso-PMMA. A for PVAc is assumed to be the same as for poly(vinyl trifluoroacetate).[8] A for P*n*BMA is not from X-ray data but via an indirect method mentioned in ref 4. [b] Multiply by 10^2 for Å^2. [c] Reference 12. [d] Calculated via eq 2 with $C = 0.0894$, using b^* values at T_{ll} from ref 12. [e] Reference 19. [f] See details in text.

reference temperature as being about $1.2T_g$ (K).

Lobanov and Frenkel have estimated T_{ll} for a variety of polymers from dielectric loss data.[18] They proposed the empirical rule $T_{ll} = T_g + 76$ K. For T_{ll} in the range 250–500 K, the numerical difference between the two empirical rules is slight.

Note: We follow several seemingly inconsistent conventions in this report. We discuss temperature variation of the Tait parameter, b, as linear in ln b–T because this is common practice in the P–V–T literature. It is also convenient for our extrapolations. At the same time, we have shown in ref 12 that $-(\mathrm{d}b/\mathrm{d}T)$ is strictly linear in T with a smaller slope above T_{ll} than below. Hence we will discuss linear correlations involving $\mathrm{d}b/\mathrm{d}T$. In all correlations with cross-sectional areas, we employ double-logarithmic plots (base 10), as has been our custom.[1-7] Moreover, experience has shown that most properties studied thus far vary as A^γ, where $0 < \gamma < 2$, and in many cases, as in this report, γ is physically meaningful.

Areas are given in Table I in nm^2 but correlations in log–log plots use Å^2 for numerical convenience. Finally, two symbols are used for the Tait parameter, b: b^* refers to values of b calculated for P from 1–400 bar and is believed to represent b as $P \rightarrow 0$, i.e., below any pressure-induced transition; b signifies a Tait parameter from the literature, with an unstated pressure range. It presumably is considered to be constant along any liquid-state isotherm or an average for that isotherm.

Table I collects values of κ at T_{ll}, which we designate κ_{ll}, areas per chain, and literature references. Most values of κ_{ll} were calculated from b^* taken from ref 12. This applies to the entries for poly(cyclohexyl methacrylate) (PCHMA), poly(*n*-butyl methacrylate) (P*n*BMA), poly(*o*-methylstyrene) (P*o*MS), polystyrene (PS), and poly(vinyl acetate) (PVAc). In some cases κ itself was available at several temperatures and could be estimated for T_{ll}. In several cases a long extrapolation of b^* to the T_{ll} region was required. These special cases are discussed individually.

Atactic Polypropylene (a-PP) and *Hevea* Rubber (*cis*-PI). Passaglia and Martin[20] reported in their Table II values of κ from +30 to -10 °C with a tabulated value at -10 °C listed in Table I. Their Figure 4 shows κ_0 as being essentially linear in temperature.

Wood and Martin[21] have determined the compressibility of unvulcanized *cis*-polyisoprene (*Hevea brasiliensis*) from 0 to 25 °C at pressures up to 500 bar. Their eq 2 indicates that κ is linear in temperature from 0 to 25 °C. We extrapolate below their measured range and calculate κ_{ll} = 3.85 cm^2/kg at -30 °C and $P = 0$. This is a relatively short and presumably dependable extrapolation.

Polyisobutylene (PIB) and Polyethylene (PE). For these three polymers, T_{ll} is far below any measured range of either κ or b^*. We preferred for extrapolation purposes to employ an expression for b vs. T above T_g first used by Gee[22] and subsequently employed extensively by Simha and his collaborators[23] as well as by Prausnitz and his group.[24] The equation is of the form

$$b = \alpha \exp(-\beta T) \tag{3}$$

with T in °C. α and β are constants for any polymer and considered valid for a stated temperature range. A collection of such constants from the literature appears in Table I of ref 12 while values calculated specifically for b^* are given in Table IV of ref 12. (b in eq 3 is presumably valid for an entire isotherm and may be different from b^*.)

Beret and Prausnitz[24] presented P–V–T data on PIB for isotherms from 52.8 to 110 °C. They found α = 1906.7 bar, $\beta = -4.1458 \times 10^{-3}$ (°C)$^{-1}$, and $C = 0.08713$. Assuming a permissible extrapolation, we estimate b at -10 °C as 1987 bar, with a calculated κ_{ll} of 4.39×10^{-5} bar^{-1}.

Beret and Prausnitz[24] provided eq 3 parameters for branched PE, while Olabisi and Simha[23] have similar parameters for both branched and linear PE's. In both instances such parameters are valid for the melt only. An extrapolation of 150 K or more to reach the T_{ll} region is of doubtful value. We calculated $\kappa_{ll} = 4.19 \times 10^{-5}$ bar^{-1} for branched PE from ref 24 and $\kappa_{ll} = 4.40 \times 10^{-5}$ bar^{-1} for linear PE from ref 23. T_{ll} is taken as -30 °C.[19]

Polybutadiene (PBD). Barlow has provided tabulated P–V–T data for PBD from 4 to 55 °C.[25a] He refers to his material as high *cis*-PBD but did not provide an analysis of isomer content. However, the specimen was designated FRS-2004 (supplied by Firestone Tire and Rubber Co. in the form of a latex).[25b] It is our belief, based on trade literature, that the material is actually a cis–trans–vinyl copolymer, with an approximate 20:63:17 ratio, a calculated T_g of about -85 °C,[26] and an estimated T_{ll} of about -45 °C. There was no evidence of a pressure-induced crystallization, which would be expected for pure *cis*-PBD.

We calculated b^* for each of the six isotherms. b^* decreased linearly with T but for extrapolation we derived the following least-squares line:

$$\ln b^* = 8.42 - 3.59 \times 10^{-3} T \text{ (K)} \tag{4}$$

$$R^2 = 0.994$$

$$\text{std error in } \ln b^* = 0.006$$

We estimated b^* = 2001 bar at -45 °C and κ as 4.47×10^{-5}

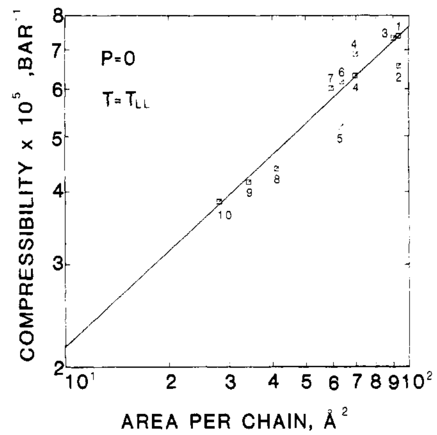

Figure 1. log–log correlation of isothermal compressibility κ, at $P \rightarrow 0$ and $T = T_{ll}$ with cross-sectional area per polymer chain in Å^2. Slope is 0.547. Regression line is given by eq 5, with the point for iso-PMMA omitted.

bar^{-1}. Equation 4 provides, to our knowledge, the first such values of b^* for PBD, as well as α and β in eq 3, although Jain and Simha obtained $\log b = 8.52 - 3.814 \times 10^{-3}T$.[27] It follows that $b \neq b^*$.

An area for mixed-isomer PBD poses a problem, even when the precise composition is known. Areas (in nm^2) for the individual components are are follows:[8] cis, 0.207; trans I, 0.179; trans II, 0.209; 1,2-syndio, 0.362; 1,2-iso, 0.432. We recommend for copolymers[2] simple additivity of areas based on weight fractions. Assuming the 1,2 component to be atactic leads to a value for $A \sim 0.22$ nm^2.

Figure 1 is a log κ_{ll} –log A (Å^2) correlation plot with a linear least-squares regression line given by

$$\log (10^5\kappa) = -0.21 + 0.55 \log A \tag{5}$$

with $R^2 = 0.934$ and the standard error in $\log (10^5\kappa_{ll}) = 0.03$. While the point for iso-PMMA is plotted in Figure 1, it was not used for the eq 5 least-squares line. The point for P*n*BMA was used. Possible sources of deviation are covered in the discussion section. PE and PBD are omitted from Table I and Figure 1 because of the long extrapolations required and/or other uncertainties.

Other Correlations

We tried in ref 12 to correlate b^* at T_{ll} with other properties of the polymer. A partially successful one was ρ^3, where ρ is density. We did not consider a correlation with area. Omitting iso-PMMA, we now obtain

$$\log b^* = 4.11 - 0.52 \log A \tag{6}$$

with A in Å^2. R^2 is 0.931 and the standard error in $\log b^*$ is 0.03. Since $b^* = C\bar{K}$, where $\bar{K}$ is the bulk modulus as $P \rightarrow 0$, it follows that $\bar{K}$ will also decrease as $A^{-0.523}$.

We also attempted in ref 12 to correlate $\mathrm{d}b/\mathrm{d}T$ with polymer properties without success. We now find that $-\mathrm{d}b/\mathrm{d}T$ above T_{ll} decreases with increasing area according to

$$\log |\mathrm{d}b/\mathrm{d}T| = 0.01 - 1.20 \log A \tag{7}$$

where the vertical bars signify the absolute value of $\mathrm{d}b/\mathrm{d}T$. iso-PMMA falls exactly on this plot whereas PS is far below the line. P*n*BMA is off, in the direction of being too high.

The corresponding plot of $-\mathrm{d}b/\mathrm{d}T$ for $T < T_{ll}$ lacks values for PIB, a-PP, and *Hevea* (*cis*-PI). The remaining polymers show considerable scatter and no recognizable pattern.

We also tried to obtain a correlation between κ and A for the glassy state, using T_g as the reference temperature. We approached T_g from both the liquid and the glassy states, although we had no glassy-state values for the low-T_g polymers. We did not find a meaningful correlation.

Discussion of Results

Figure 1 and eq 5 state that κ_{ll} is almost directly proportional to an average intermolecular distance given by $A^{0.54}$. This is intuitively appealing. Moreover, it is consistent with observations of Miller et al.[28] based on amorphous halo data by X-ray scattering at 20 °C and particularly on an intersegmental distance which increases with $A^{0.6}$. This study suggests that polymer chains in the amorphous state can be visualized as cylinders in a hexagonal array.[28]

An area for PCHMA was not available in ref 8 from lattice parameters. However, PCHMA was investigated in ref 28a. It gave a well-defined amorphous halo corresponding to an area of 0.934 nm^2 [28b] as listed in Table I and plotted in Figure 1.

We have shown[29] that area per chain increases linearly with M_0/Z_0, where M_0 is the molecular weight per monomer unit and Z_0 is the number of in-chain atoms per monomer unit. Hence, the larger the substituents on a chain, the greater is the area per chain needed to satisfy van der Waals requirements for closest approach of atoms.

As we have shown, chain stiffness, σ, increases with area per chain,[5] presumably as a result of steric hindrance between next nearest neighbors along the chain. This effect tends to cause segments of the chains to approximate the packing of cylinders discussed earlier. The further apart these "cylinders" are, the greater is the liquid-state compressibility, κ, and the lower is the bulk modulus, $\bar{K}$.

We have also tried a correlation between κ at $T_g + 100$ K and area. The equation of the least-squares line is

$$\log (10^5\kappa)(T_g + 100\ \mathrm{K}) = -0.04 + 1.01 \log A \tag{8}$$

with $R^2 = 0.856$ and the standard error in $\log \kappa = 0.05$. This is clearly a poorer and much different type of correlation than that for κ_{ll} given earlier. It seems to justify our choice of T_{ll} as a standard reference temperature for the liquid state.

Some comments about scatter in Figure 1 are in order. As noted in the Introduction, values of A refer to the crystalline state at room temperature. T_{ll} for the first seven polymers is well above room temperature so that a substantial correction for thermal expansion would be appropriate, especially for PS, PoMS, PMMA, and PCHMA. Values of b for PE were determined in the temperature range 140–200 °C. An approximate correction for liquid-state coefficients of thermal expansion, α_l, would presumably be the Simha–Boyer empirical rule, $\alpha_l T_g = 0.167$.[30] There is a strong tendency for α_l to increase from right to left in Figure 1. This tendency would be even more pronounced if PE and PBD were included. T_g decreases from right to left. PMMA is about 50 K above a trend line, and P*n*BMA is about 80 K below.

Finally, there is one other systematic trend hidden in Figure 1. The ratio of amorphous density to crystalline density, ρ_a/ρ_c, increases with area[31] as

$$\rho_a/\rho_c \sim A^{0.18} \tag{9}$$

rather than having an average value of about 0.9 as stated in the Introduction. Actually, this ratio is close to 0.86 for PE, which is on the eq 9 trend line. iso-PMMA is an exception since its ratio is very close to unity.[32] This is a consequence of a high degree of stereoregularity (0.99 according to Quach et al.[33]) and hence near perfect packing even in the amorphous state. This fact probably accounts

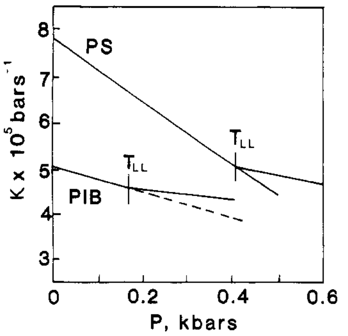

Figure 2. Calculated κ–P lines at T_{ll} + 30 K for polystyrene and polyisobutylene showing abrupt slope changes at T_{ll}' and T_{ll}.

for the relatively low value of κ_{ll} in Figure 1.

Figure 1 has clarified one feature about isothermal V–P data that had long puzzled us. We demonstrated with isobaric V–T data at P = 1 bar that T_{ll} is very weak for both PS and PoMS,[14] and yet T_{ll} showed up very clearly in isothermal V–T calculations.[10,34] At the same time, T_{ll} for PIB was weak in isothermal V–P data[10] (no thermal expansion data near T_{ll} were found for PIB). The very high values of κ for PS and PoMS, especially at $P \rightarrow 0$, suggest that volume changes with pressure can be determined with much greater accuracy for these two polymers than for one like PIB.

Figure 2 shows calculated values of κ at T_{ll} (at P = 0) + 30 K as a function of pressure, using an expression derived from eq 2

$$d\kappa/dP \sim \kappa(P = 0)/b^* \qquad (10)$$

PS and PIB were selected for illustration. Since κ increases with A while b^* decreases and since dT_{ll}/dP varies inversely with T_g,[10,11] there is a compensating effect noted in Figure 2. Even so, volume changes with pressure faster for PS than for PIB.

Figure 3 shows a running first derivative for an anionically prepared PS of $\bar{M}_n$ = 20 400 at 196.6 °C. The data are that of Oels and Rehage with pressure intervals of 50 bar from P = 100 to P = 1000 bar and 100 bar from P = 1000 to P = 3000 bar.[35] The ordinate is $V_0\kappa$. A small slope change at T_{ll}' is followed by a larger change at T_{ll}. This confirms an earlier finding of T_{ll}' and T_{ll} with this set of data, using two approximate forms of the Tait equation. (See Figure 5 of ref 10.) We have estimated T_{ll} for this polymer to be 144 °C at P = 0.[34] Figure 3 reflects a high κ, resulting from large A plus a further enhancement of κ by the large temperature interval above T_{ll} at P = 0. In contrast, T_{ll} in PS is just barely detectable by thermal expansion at P = 1 bar.[14] Attention is directed to a recent study[36] that did not detect either a $T > T_g$ or a $T < T_g$ event in a P–V–T study of PS. We ascribe this to a very fast pressurization procedure without pauses for volume equilibrium, in contrast to the practice employed by Oels and Rehage of slower increases in pressure and time delays between incremental pressures.

Summary and Conclusion

We have demonstrated for a series of ten polymers for which P–V–T results were available in the literature that isothermal compressibility, κ (bar^{-1}), at $P \rightarrow 0$ and $T = T_{ll}$ increases with cross-sectional area, A, per polymer chain as $A^{0.547}$, i.e., approximately as an average interchain distance. The isothermal bulk modulus, $\bar{K}$, at the same temperature and $P \rightarrow 0$ decreases as $A^{-0.52}$. The Tait equation parameter, b^*, for $P \rightarrow 0$ and $T = T_{ll}$ likewise decreases as $A^{-0.52}$, as it must since $\bar{K} = b^*/C$, where C is a constant.

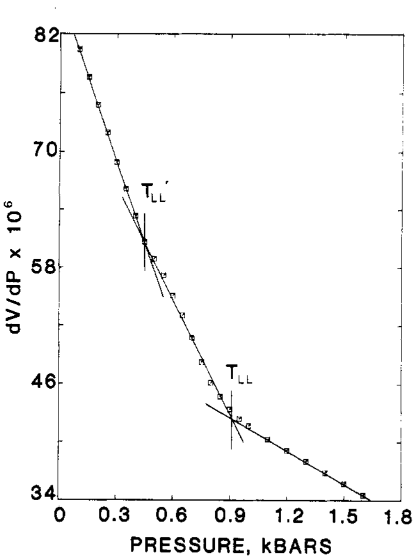

Figure 3. Running first derivative, $\Delta V_{sp}/\Delta P$, at T = 196.6 °C for PS of $\bar{M}_n$ = 20 400, showing T_{ll}' and T_{ll}. Data of Oels and Rehage.[35] The ordinate is $V_0\kappa$ but V_0 is very close to unity.

Areas range from 0.280 nm^2 for *Hevea* rubber to 0.94 nm^2 for P*n*BMA, with κ ranging from 3.84 × 10^{-5} to 7.39 × 10^{-5} bar^{-1}. Points for iso-PMMA and P*n*BMA fall below the log κ–log A trend line. Points for PE and PBD are not plotted but would lie above the trend line. This latter could be a result of long extrapolations and/or failure to correct for thermal contraction and/or ρ_a/ρ_c.

One attempt at a different liquid-state reference temperature, namely, T_g + 100 K, resulted in an inferior correlation of κ with A.

High values of κ for polymers of large A such as PS and PoMS should facilitate location of weak liquid-state transitions, especially with temperatures well above T_{ll} at P = 0.

Appendix

One of the reviewers has noted that Plazek[37] considered T_{ll} and T_{ll}' as not being thermodynamic transitions, with which we agree. Hence this reviewer questions our analysis of P–V–T data to locate these $T > T_g$ temperatures. Plazek also notes[37] with equal clarity that T_g is not a thermodynamic transition, although it is commonly called a transition and treated as such. As we have noted on various occasions,[15,16] both T_g and T_{ll} are observed by kinetic methods (dynamic mechanical and dielectric loss) as well as by quasi-static methods such as thermal expansion and specific heat. Because of this common behavior and also the empirical finding[15] that T_{ll}/T_g = 1.20 ± 0.05, we tend to refer to T_{ll} by either or both of two terms: transition (relaxation). The same P–V–T data analysis used in this paper in the T_{ll} region has been employed for years in the T_g region. In any event we neither assume nor claim that T_{ll} is a thermodynamic transition.

Registry No. PCHMA, 25768-50-7; P*n*BMA, 9003-63-8; PoMS, 25087-21-2; PS, 9003-53-6; iso-PMMA, 25188-98-1; a-PMMA, 9011-14-7; PVAc, 9003-20-7; PIB, 9003-27-4; a-PP, 9003-07-0; *cis*-PI, 9002-88-4.

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Effect of Polyelectrolytes on the Rate of Ligand–Metal Ion Reactions. 3. Role of Hydrophobic Interactions between Ligand and Polyelectrolyte

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ABSTRACT: The part played by the hydrophobic interactions in the polyelectrolyte "catalysis" of some ligand–metal ion (Ni(II) and Co(II)) complex formation is investigated (i) by changing the substituent groups of the ligand (pyridylazo compound) and (ii) by using as polyelectrolytes, copolymers of methacrylic acid and styrene with varying amounts of styrene. The maximum "catalysis" effect is shown to be very dependent on the hydrophobic character of both the ligand and the polyelectrolyte. The polyelectrolyte concentration giving the maximum effect is generally related to the complete condensation of divalent ions as can be predicted from Manning's theory, whereas the amplitude of the effect is related to the strength of the hydrophobic interaction between the ligand and the polyelectrolyte. An improved model is proposed on the basis of the present results to interpret the acceleration effect of hydrophobic polyelectrolytes.

Introduction

Since the pioneering work of Morawetz and co-workers,[1–4] the polyelectrolyte "catalysis" of chemical reactions involving ionic species has been the object of numerous papers in the last years[5–34] (the list given in References and Notes is far from being exhaustive).

Some applications of such a property of charged polymers have also been put forward dealing with the possibility of performing the necessary charge separation in photoelectron-transfer reactions where hydrogen production is expected.[35–37] The mechanisms responsible for the effect of polyelectrolytes are complex and their complete understanding calls for new experiments.

Extensive work on this subject has been particularly performed by Ise and co-workers,[5–23] who have added new insight to this field by investigating the role of solvation and desolvation of the reactants and activated complexes.[16–23]

For our part, we have been concerned in previous papers with the effects of polyanions on some complexation reactions between a pyridylazo ligand and divalent transition-metal ions.[31–33] A rate-accelerating effect has been shown to occur in the presence of sodium poly(styrenesulfonate)[31,32] whereas a rate-retarding effect occurs with sodium polyphosphate.[31,33] As both polyelectrolytes are of the anionic type and, furthermore, are characterized by the same charge parameter, there was no possible interpretation without taking into account specific interactions between the divalent metal ion and the polyanion on the one hand and the hydrophobic interactions between the ligand and the polymer when they may occur, on the other hand.

The purpose of the present investigation is to define the part played by the hydrophobic interactions. Two different approaches have been considered: (i) the influence of the hydrophobic character of the ligand has been investigated by changing the substituent groups of the pyridylazo radical; (ii) the influence of the hydrophobic character of the polyelectrolyte has been studied by using copolymers of methacrylic acid and styrene with varying amounts of styrene.

Experimental Section

Materials. The pyridylazo compounds obtained from the following sources were used without further purification: *N*,*N*-dimethyl-4-(2-pyridylazo)aniline (PADA) from Sigma, 4-(2-pyridylazo)resorcinol (PAR) and 1-(2-pyridylazo)-2-naphthol (β-PAN) from Fluka. Stock solutions of concentration 2.5×10^{-4} M were prepared in water acidified with HCl for PADA and PAR

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