Variation of chain volume with conformation

The origin of the non-zero value of the parameter γ may be found in the variation of chain volume with conformation. Since $\overline{r_i^2}$ is proportional to $V_0^{2/3}$ and is independent of the current volume V the γ-parameter can be expressed as

$$\gamma=(\partial \ln \overline{r_o^2}/\partial \ln V)_{TL}=(\partial \ln \overline{r_o^2}/\partial P)_{TL}(\partial P/\partial \ln V)_{TL} \qquad (2)$$

where the last term on the right-hand side, B, is related to the isothermal bulk modulus of the network. Generally, the temperature dependence of $\overline{r_o^2}$ reflects the difference in energy between more and less extended conformations whereas the pressure dependence reflects a similar difference in volume[3]. So far, it has been tacitly assumed in configurational statistics that the effective volume of various chain conformations is the same. However, there is increasing experimental and theoretical evidence that the volume of rotational isomers in the chain may apppreciably differ. For example, in linear alkanes the trans conformer at rotation around C–C bond exhibits the highest volume, i.e. the extended all-*trans* zig-zag form of a molecule has the maximal molecular volume. Various experimental techniques indicate[4] that the *gauche–trans* difference of van der Waals volume, ΔV_w, is about -1.5 cm^3 mol^{-1} and the theoretical methods predict an even higher value (-2.5 cm^3 mol^{-1})[4].

The difference in molecular volume of chain conformations has a remarkable influence on the conformational equilibrium of a chain in the condensed phase environment regarded as a continuum[4,5]. Since the volume of a molecule changes at internal rotation, the work $P_i \Delta V_w$ has to be done to displace the surrounding continuum where P_i is the internal pressure. The term $P_i \Delta V_w$ affects the potential of internal rotation and diminishes the *gauche–trans* energy difference ΔE in the case of alkanes[5]. Accordingly, an increase of internal or external pressure should increase the number of *gauche* bonds and the n-alkane molecule should be more globular as has also been confirmed experimentally[6].

An introduction of pressure-dependent statistical weight factors has been advocated[4] to account for the pressure effect on the configurational properties of chains. In that way the variation of mean chain dimensions with pressure and the quotient $\mathrm{d}\ln \overline{r_o^2}/\mathrm{d}P$ similar to that in equation (2) can be determined from the calculations developed by Flory[7].

Estimation of parameter γ for nonpolar network

Let us estimate the value of parameter γ for typical nonpolar network as represented by the crosslinked polymethylene (PM) chains by calculation of the quotient $\mathrm{d}\ln \overline{r_o^2}/\mathrm{d}P$ for PM. Configuration-dependent properties of PM were rationalized by using two statistical weight factors σ and ω[7]. The σ factor is connected with the *gauche–trans* energy difference, ΔE, and ω accounts for the energy, ΔE_ω, of two adjacent *gauche* isomers with severe steric overlap. The dependence of statistical weights on pressure leads to the pressure-dependent mean chain dimensions of PM. They are usually expressed by the characteristic ratio $C=\overline{r_o^2}/nl^2$, where n is the number of segments in a polymer chain, and l is the length of each segment. Besides the energy parameters C depends slightly on the C–C–C angle in the chain, θ, and on the localization of the *gauche* minima on the potential of internal rotation, φ[7]. Let us assume that pressure affects only the statistical weight σ through relation

$$\sigma=\exp(\Delta E-P\Delta V_w)/RT$$

Applying pressure of 200 MPa (about 2000 atm) the recommended ΔE value[7] 2.1 kJ mol^{-1} is reduced by 0.5 kJ mol^{-1} provided the estimation of volume difference $\Delta V_w = -2.5$ cm^3 mol^{-1} from the previous paper[4] is used. Using the values $T=413$ K, $\theta=112°$, $\varphi=\pm 120°$, $\Delta E_\omega = 8.4$ kJ mol^{-1} characteristic ratio for PM changes from 6.87 at normal pressure to about 6.4 representing the situation at $P=200$ MPa. In other words, the mean unperturbed chain dimensions, $\overline{r_o^2}$, at 200 MPa decreased by a factor of 1.073. No experimental data are available concerning the pressure effect on the dimensions of PM in solution. However, a comparison with the experimental results for other polymers in solution[8-10] suggests that the pressure coefficient $(\mathrm{d}\ln \overline{r_o^2}/\mathrm{d}P) = -3.55.10^{-10}$ Pa^{-1}, following from our calculations, is reasonable. The effect of pressure on the chain dimensions of PM is parallel to that of temperature. In both cases the coefficient is negative since an increase of temperature or pressure brings about a higher population of the *gauche* states and the coiling of PM chains.

The similar pressure effect can also be assumed for other nonpolar hydrocarbon polymers in solution, in which V_w (*gauche*) $< V_w$ (*trans*) for rotation about C–C bond. The pressure effect on conformational equilibria is undoubtedly also important for polar systems but the analysis is inevitably complicated by the presence of the specific solvent effect on the torsional potentials and electrostriction phenomena. In addition, it should be noted that generally at rotation about single bonds, V_w (*gauche*) is not always smaller than V_w (*trans*).

We assume that the pressure coefficient -3.55×10^{-10} Pa^{-1} calculated for PM chains in unperturbed state corresponds to the quotient $(\partial \ln \overline{r_o^2}/\partial P)_{TL}$ in a network. At least in a highly crosslinked swollen network this approximation should hold.

Because of the high value of the second term B on the right-hand-side of equation (2), even small changes of reference dimensions with pressure as calculated for PM may result in a fairly large value of the parameter γ. as an example the value -1.93×10^9 Pa determined for another typical nonpolar network — natural rubber[11]. The substitution of these values into equation (2) yields for γ the value of 0.68. A comparable magnitude of γ parameter was determined for several rubbers by various authors[2,12,13]. In direct experimental measurements of pressure variation of the G modulus (which should reflect the $\overline{r_o^2}$ changes with P) even more conspicuous changes were observed such as 7.5% increase of the G modulus of natural rubber at 100 MPa[2,14].

The proposed explanation of the origin of the parameter γ is certainly an oversimplification but it properly emphasizes the importance of steric and packing forces for the equilibrium of rotational isomers in the chains of typical nonpolar rubbery network. The pressure effect resembles the specific (dielectric) solvent effect observed in polar polymer networks at normal pressure[15]. As noted above, external or internal pressure changes in polar networks may influence r_o^2 not only due to the volume difference of the rotational isomers but also because of the pressure variation of dielectric interactions.

The illustrative calculation confirms that even a minute change of reference chain dimensions with pressure has an important outcome for thermodynamic analysis of rubber elasticity. As was pointed out by Staverman[3] this effect is important even though the macroscopic volume changes of the sample during deformation can safely be neglected. The postulate about the exclusively intramolecular origin of rubber elasticity is invalidated in networks under strong pressure where the intermolecular packing and steric forces play a significant role and thermodynamic relations for the force f have to be modified by additional term containing parameter $\gamma^{1,2,15}$. Further, the results indicate the necessity of more detailed investigation of pressure-volume configurational properties of polymer chains unperturbed by long-range interactions. Neglect of the pressure or volume as variables in chain statistics might not be so warranted as is generally believed. Finally, it should be pointed out that similar reasoning as presented above can also be invoked in explanation of the change in polymer conformation with pressure in amorphous glassy polymers[16].

References

1 Tobolsky, A. V. and Shen, M. *J. Appl. Phys.* 1966, **37**, 1952
2 Shen, M. and Croucher, M. *J. Macromol. Sci.-Revs.* 1975, **C12**, 287
3 Staverman, A. J. *J. Polym. Sci.* 1975, **37**, 1952
4 Bleha, T. *Makromol. Chem., Rapid Commun.* 1981, **2**, 35
5 Bleha, T., Gajdos, J. and Tvaroska, I. *J. Molec. Struct.* 1980, **68**, 189
6 Shoen, P. E., Priest, R. G., Sheridan, J. P. and Schnur, J. P. *J. Chem. Phys.* 1979, **71**, 317
7 Flory, P. J. Statistical Mechanics of Chain Molecules, Interscience, New York, N.Y., 1969
8 Hammel, G. L., Schulz, G. V. and Lechner, M. D. *Eur. Polym. J.* 1979, **15**, 209
9 Gaeckle, D. and Patterson, D. *Macromolecules* 1972, **5**, 136
10 Kubota, K., Kubo, K. and Ogino, K. *Bull. Chem. Soc. Japan* 1976, **49**, 2410
11 Wolf, F. P. and Allen, G. *Polymer* 1975, **16**, 209
12 Sharda, S. C. and Tschoegl, N. W. *Macromolecules* 1976, **9**, 910
13 Godovsky, Yu. K. *Polymer* 1981, **22**, 75
14 Patterson, M. S. J. Appl. Phys., 1964, **35**, 176
15 Vasko, M., Bleha, T. and Romanov, A. *J. Macromol. Sci.-Revs.* 1976, **C15**, 1
16 O'Reilly, J. M. and Mosher, R. A. *J. Polym. Sci., Polym. Lett. Edn.* 1979, **17**, 731

Block copolymers synthesis *via* anionic to Ziegler–Natta transformation reaction

P. Cohen, M. J. M. Abadie and F. Schué
Laboratoire de Chimie Macromoleculaire, USTL, 34060 *Montpellier Cedex, France*

and D. H. Richards
*PERME, Ministry of Defence, Waltham Abbey, Essex EN*9 1*BP, UK*

(*Received* 24 *June* 1981)

Introduction

A new approach has been developed in recent years to the synthesis of block copolymers involving novel combinations of monomers. This has required devising transformation reactions to enable the mode of polymerization employed for the first monomer to be switched to a different mode most suitable for polymerizing a second monomer. Such processes require an intermediate stage where the initial homopolymer may be isolated before being introduced into an environment appropriate to the polymerization of the second monomer. Examples have been published of the following transformation reactions: anion to cation[1-4], anion to free radical[5-8], and cation to anion[9], and the subject has been recently reviewed[10]. Other transformations are currently being studied, and this publication is a preliminary report of an approach to the transformation from anion to Ziegler–Natta (ZN) catalysis.

ZN catalytic systems were defined as a combination of metal alkyls of Groups I to III with transition metal salts of Groups IV to VIII[11,12]. In practice, very efficient catalyst combinations are derived from the interaction of aluminium or lithium alkyls with titanium, vanadium or cobalt salts, and in this study, investigation has been confined to catalysts involving titanium III or IV as a component.

The classical interpretation of the mode of reaction between aluminium alkyl and a titanium IV salt is initially one of reduction of the latter to titanium III (equations 1 and 2), the alkyl radical generated being eliminated by termination.

$$\mathrm{TiCl_4 + R_3Al \rightarrow RTiCl_3 + R_2AlCl} \tag{1}$$

$$\mathrm{RTiCl_3 \rightarrow \beta TiCl_3 + R\cdot} \tag{2}$$

Further alkylation of the titanium III salt then occurs to generate the titanium species capable of initiating polymerization of monomers such as ethylene (equations 3 and 4). When the alkyl group is small (e.g. ethyl), such catalytic systems are insoluble in normal solvents such as hexane, but increase in the size of the ligand leads to increased solubility with retention of catalytic activity[13]. An analogous set of reactions applies to the formation of catalysts from the interaction of lithium alkyls and titanium salts.

$$\mathrm{\beta TiCl_3 + R_3Al \rightarrow RTiCl_2 + R_2AlCl} \tag{3}$$

$$\mathrm{RTiCl_2 + C_2H_4 \rightarrow \underset{\text{coordination}}{RTiCl_2.C_2H_4} \rightarrow \underset{\text{insertion}}{RCH_2CH_2TiCl_2}} \tag{4}$$

Since the alkyl ligand is incorporated in the final polymer produced (equation 4), it seemed feasible that the

0032-3861/81/101316-04$02.00