THE CHARACTERISTIC RATIO OF BUTADIENE–STYRENE AND BUTADIENE–ACRYLONITRILE COPOLYMERS

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Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

A method advanced recently is used to estimate the characteristic ratio C^∞ for statistical butadiene–styrene and butadiene–acrylonitrile copolymers from the reported data of the limiting viscosity number and sedimentation coefficient. The results are compared with those of the traditional methods. The dependences of C^∞ on the copolymer composition are discussed and interpreted in terms of steric and/or dipole-dipole interactions of adjacent monomeric units.

The properties of polymeric materials in bulk are largely dependent on the configuration of constituent macromolecules. Thus, the study of solution properties which provide some configurational characteristics (*e.g.*, unperturbed dimensions, dipole moments) have become a matter of more than academic interest.

The quantity most frequently used in such studies is the characteristic ratio[1], C^∞,

$$C^\infty = \overline{R_0^2}/nl^2 \,. \tag{1}$$

Here, the symbol $\overline{R_0^2}$ stands for the mean-square end-to-end distance of a real polymer chain in the random-coil configuration unperturbed by the excluded-volume effect. The product nl^2 is the same quantity for a hypothetical freely jointed chain composed of n skeletal bonds, each[1] of length l. The characteristic ratio can be calculated from the experimentally obtained values of $\overline{R_0^2}/M$ by means of the equation

$$C^\infty = (\overline{R_0^2}/M)\,(M_0/l^2)\,, \tag{2}$$

where M is the polymer molar mass and M_0 is the mean molar mass per skeletal bond.

In a recent paper[2], we have proposed a new method for evaluating $\overline{R_0^2}/M$ from a combination of the limiting viscosity number and the sedimentation coefficient, both measured under θ-conditions (*i.e.* at a temperature where the second virial coefficient is zero). The procedure has some advantages over the more usual methods, and seems therefore well suited for a study of systems where the estimation of some basic molecular characteristics (*e.g.*, molar mass) or the preparation of fractions with narrow molar-mass distribution is impeded by severe experimental difficulties. Copolymers of butadiene with styrene or acrylonitrile, *i.e.* well-known rubber-like materials are examples of such systems.

In the present paper the method is applied to hydrodynamic data for these systems and the results are compared with those obtained in a more traditional way. The data originate from several papers[3-10]. A part of them was discussed by Poddubnyi and Podalinskii several years ago[11]. As new data have since been published[6,10] and the method described in ref.[2] offers an independent check, we believe that an analysis of all data available will provide representative values of C^{∞} as a basis for discussion of the configuration of these substances.

METHODICAL

The method described in ref.[2] is based on the equation

$$[\eta]_0/s_0 = N_A\eta_0/(1 - \bar{v}\varrho_0)\,\Phi_0 P_0(\overline{R_0^2}/M)^2\,, \qquad (3)$$

where $[\eta]_0$ is the limiting viscosity number (in cm^3/g) and s_0 is the sedimentation coefficient (in s), both measured under Θ-conditions. The symbols η_0 and ϱ_0 stand, respectively, for the solvent viscosity and density, $\bar{v}$ is the partial specific volume of the solute, N_A is the Avogadro number, and $\Phi_0 P_0$ is the product of universal parameters ($\Phi_0 P_0 = 1{\cdot}49 \,.\, 10^{24}\ mol^{-1}$).

The advantages of this method may be summarized in the following terms[2]: *i*) The uncertainty in the individual values of P_0 and Φ_0 almost vanishes from their product; *ii*) no data on molar mass are needed; *iii*) the resulting value of $\overline{R_0^2}/M$ is unaffected by polydispersity.

The difficulties of obtaining the mass-average molar mass, M_w, for butadiene copolymers by the light-scattering method are well known[6,12,13]. They are due to the presence of large particles (microgels, powdery admixtures from the copolymerization system) which are seldom completely removed even by a multistage purification. Hydrodynamic methods (*e.g.*, combination of sedimentation and diffusion, the Archibald method) yield M_w values of the molecularly dispersed copolymer but are time-consuming. The above difficulties are not eliminated by fractionation. Moreover, in a fractionation procedure the polymer substance is exposed to a danger of chemical change (oxidation, crosslinking, *etc.*). The method based on Eq. (*3*) overcomes these difficulties. On the other hand, there are some other difficulties, inherently connected with these systems, which cannot be removed by the new treatment.

Homopolymers and copolymers of butadiene are usually branched. Branching increases with an increase in the molar mass and/or in the conversion of copolymerization. For such systems, the values of $[\eta]_0/s_0$ are not constant over the whole span of the molar mass. In order to derive a configurational characteristic for linear chains, much attention is to be paid to the treatment of data.

The butadiene–acrylonitrile copolymers are composed of polar and non-polar constitutional units so that the θ-conditions can be found in mixed solvents only. This is a disadvantage because some contributions to the limiting viscosity number in mixed solvents arise from reasons not connected with chain configuration and affect the values of $[\eta]$[14].

The results of the treatment based on Eq. (*3*) are compared with those evaluated from the viscosity constant[1] K_0,

$$K_0 = \Phi_0(\overline{R_0^2}/M)^{3/2} \tag{4}$$

which can be obtained from the $[\eta]_0$ data according to

$$K_0 = [\eta]_0/M^{1/2} \tag{5}$$

or from the limiting viscosity numbers $[\eta]$ in a good solvent by eliminating the excluded-volume effect in an appropriate way. The Stockmayer–Fixman–Burchard method[15,16], *i.e.* the extrapolation to $M^{1/2} = 0$ of the plot of $[\eta]/M^{1/2}$ *vs* $M^{1/2}$, is used as the most convenient.

RESULTS AND DISCUSSION

Estimation of $\overline{R_0^2}/M$

For linear polymer chains in the random-coil configuration, the values of $[\eta]_0/s_0$ should be independent of molar mass. With some of the butadiene–styrene (SBR) and butadiene–acrylonitrile (ABR) copolymers discussed in this paper (Figs 1*a*, 2), these values are indeed constant (within 10%) up to high values of molar mass, whereas with others a downward curvature sets in at rather low values of M ($50 \cdot 10^3$ to $250 \cdot 10^3$). In the latter case, the initial (approximately horizontal) part of the plots of $[\eta]_0/s_0$ *vs* $M^{1/2}$ was used to estimate $\overline{R_0^2}/M$ for linear chains.

The values of $(1 - \bar{v}\varrho_0)$ and η_0 needed in calculations of $\overline{R_0^2}/M$ according to Eq. (*3*) were taken from the original papers or recalculated by means of the Svedberg or Mandelkern–Flory equations from published values of s_θ, D_0 and $[\eta]_\theta$.

The plots of $[\eta]_\theta/M^{1/2}$ *vs* $M^{1/2}$ (Figs 1*b* and 3) are similar to those in Figs 1*a* and 2. With the ABR copolymers, which were measured in mixed solvents, the solvent effect on K_0 is noticeable but usually less than 5%. Only the copolymers with a low content of butadiene monomeric units are an exception; the difference in $[\eta]_0$ and K_0 for two mixed θ-solvents amounts to about 10% (Fig. 3).

To complete the results for ABR, one value of K_0 (for the mole fraction of butadiene constitutional units $x_B = 0{\cdot}66$) was obtained by means of the Stockmayer–Fixman–Burchard plot ($[\eta]/M^{1/2}$ *vs* $M^{1/2}$) from the limiting viscosity numbers in toluene[7] for fractions characterized by the number-average molar mass M_n. The plot was smooth and can be extrapolated to $M^{1/2} = 0$ without problems. The result is surprisingly low, and a correction for polydispersity (which is not known) would decrease it even more.

The composition of all SBR samples is nearly the same ($x_B = 0{\cdot}82 - 0{\cdot}85$), and so are the θ-temperatures ($21 - 24$°C). One would expect a better agreement in K_0 (after appropriate corrections for polydispersity) than that actually found.

Homma and Fujita[3,4] measured several fractions of SBR (characterized by M_n) in 2-pentanone and found $K_0 = 0{\cdot}18$ (broken line 2 in Fig. 1*b*). An approximate correction for polydispersity reduces the value to 0·17. The value deduced from our

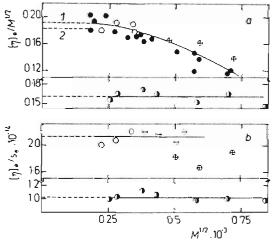

FIG. 1

Determination of $\overline{R_0^2}/M$ from the hydrodynamic data for butadiene–styrene copolymers: (*a*) Plot of $[\eta]_0/M^{1/2}$ *vs* $M^{1/2}$. (*b*) $[\eta]_0/s_0$ *vs* $M^{1/2}$. Mole fraction of butadiene constitutional units, $x_B = 0{\cdot}82 - 0{\cdot}85$. Data points for 2-pentanone: ● non-fractionated samples[6] (M_w); ○ linear fractions (M_n), ⊕ non-linear fractions (M_n), ⊖ non-fractionated samples[3,4] (M_η). Data points for octane: ◑ fractions[5] (M_{sD}). For θ-temperatures, see Table I

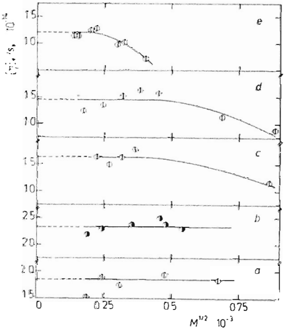

FIG. 2

Determination of $\overline{R_0^2}/M$ for butadiene–acrylonitrile copolymers according to Eq. (*3*). Mole fraction of butadiene constitutional units x_B: (*a*) 0·62 (ref.[10]), (*b*) 0·82 (ref.[9]), (*c*) 0·72 (ref.[9]), (*d*) 0·60 (ref.[8]), (*c*) 0·45 (ref.[9]). Mixed θ-solvents: butanone/cyclohexane ⊕; butanone/2-propanol ◑. For composition of mixed solvents and θ-temperatures, see Table I data[6] in the same solvent for nonfractionated samples (covering a broad range of copolymerization conversion from 10 to 70%) is higher by about 10% ($K_0 = 0{\cdot}19$), and since it is essentially $[\eta]_0/M_w$, it would be increased (though slightly) by a correction for polydispersity.

Poddubnyi and coworkers[5] estimated K_0 from the $[\eta]_0$-values in octane ($K_0 = 0{\cdot}16$). Since fractions and M_{sD} values were used in that study, the polydispersity correction would be very low and would not shift the result closer to the values mentioned above.

The differences in $\overline{R_0^2}/M$ calculated by means of Eq. (*4*) are lower than those in K_0 (Table I) but remain noticeable. We are not able to offer a plausible explanation.

Characteristic Ratio

The mean chain repeating unit of the butadiene–styrene or butadiene–acrylonitrile copolymers is composed of m_A styrene (or acrylonitrile) and m_B butadiene units, and comprises m_B double bonds and $(2m_A + 3m_B)$ single bonds (provided only the 1,4-addition takes place during copolymerization). The mean-square bond length, $\overline{l^2}$, to be substituted into Eq. (*2*) when calculating C^∞, is

$$\overline{l^2} = [m_B l_b^2 + (2m_A + 3m_B)\, l_a^2]/(2m_A + 4m_B)\,, \qquad (6)$$

where l_a and l_b are the lengths of the single and double bonds, respectively ($l_a = 0{\cdot}153$ nm, $l_b = 0{\cdot}134$ nm). The mean molar mass per skeletal bond, M_0, is

$$M_0 = (m_A M_A + m_B M_B)/(2m_A + 4m_B)\,, \qquad (7)$$

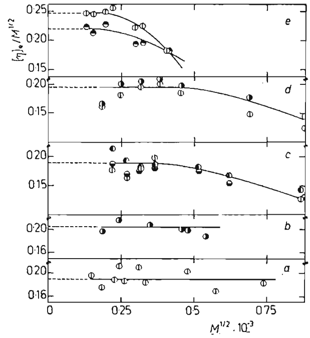

FIG. 3

Determination of the K_0 constant for butadiene–acrylonitrile copolymers. Designation of samples as in Fig. 2. Mixed θ-solvents: butanone/cyclohexane ⦶; butanone/2-propanol ◑; acetone/2-propanol ◐; dimethylformamide/2-propanol ◓; benzene/heptane ◒. For composition of mixed solvents and θ-temperatures, see Table I

TABLE I

Configurational characteristics of butadiene–styrene and butadiene–acrylonitrile copolymers ($\overline{R_0^2}/M$ in nm^2 g^{-1} mol). x_B is the mole fraction of butadiene monomeric units. Basic data from the original papers (refs[3–10])

x_B	Calc. from $[\eta]_0/s_0$		Calc. from K_0		Solvent (composition vol.%)	T_0, °C	Ref.
	$(\overline{R_0^2}/M) . 10^2$	C^∞	$(\overline{R_0^2}/M) . 10^2$	C^∞			
			Butadiene–styrene				
0·85	0·85	6·4	0·76[a]	5·7	2-pentanone	21	3, 4
0·85			0·81	6·1	2-pentanone	21	6
0·82	0·74	5·8	0·73	5·7	octane	21	5
			Butadiene-acrylonitrile				
0·82	0·93	5·95	0·85	5·4	butanone/2-propanol 59 : 41	20	9
0·72	0·83	5·46	0·78	5·2	butanone/cyclohexane 36 : 64	21	9
0·72			0·82	5·4	propane/2-propanol 61·5 : 38·5	21	9
0·72			0·78	5·2	benzene/heptane 81·5 : 18·5	19	9
0·66			0·74	5·0	toluene	—[b]	7
0·62	0·96	6·50	0·81	5·5	butanone/cyclohexane 47·5 : 52·5	25	10
0·60	0·85	5·80	0·81	5·5	butanone/cyclohexane 47·5 : 52·5	25	8
0·60			0·85	5·8	butanone/2-propanol 60 : 40	20	8
0·45	1·07	7·66	0·97	6·9	butanone/cyclohexane 76 : 24	21	9
0·45			0·90	6·4	dimethylformamide/2-propanol 48 : 52	38	9

[a] Corrected for polydispersity (see text), [b] Estimated from good-solvent data by means of the Stockmayer–Fixman–Burchard method.

where M_A is the molar mass of styrene or acrylonitrile (104 or 53 g mol^{-1}, respectively), and $M_B = 54$ g mol^{-1} is the molar mass of butadiene.

The values of C^∞ calculated according to Eqs (*2*), (*6*) and (*7*) are collected in Table I and plotted in Fig. 4 against the copolymer composition. The C^∞ values in the lower part were obtained according to Eq. (*3*), those in the upper part were calculated from K_0. The former are systematically higher by a few per cent. The sign and size of the differences seem consistent with the effect of polydispersity on the values of K_0.

The characteristic ratio of binary copolymers depends on the chemical nature and the relative content of monomer units, and on their sequential and configurational arrangement[17]. Developing the idea of Stockmayer and coworkers[18], Kotaka and coworkers[19] have proposed a simple formula for the characteristic ratio of an "ideal" copolymer in which no extra interaction takes place between neighbouring unlike monomer units:

$$C^\infty = C_A^\infty x_A + C_B^\infty x_B . \qquad (8)$$

Here, C_i^∞ (with i = A, B) are the characteristic ratios of the parent homopolymers and x_i are the mole fractions of the monomeric units. The linear dependence of C^∞ on x_i can be taken as a reference line, and the deviations from linearity in real systems give evidence of some additional interactions. Positive deviations (which occur more frequently in systems studied so far) are assigned to the repulsive interactions being increased by the contribution of dyads of unlike monomer units, whereas negative deviations are associated with a relaxation of repulsion or with attractive interactions.

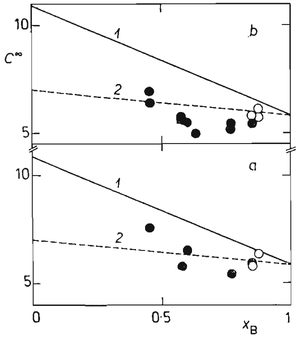

FIG. 4

Characteristic ratio C^∞ as a function of composition of the butadiene–styrene and butadiene–acrylonitrile copolymers. (*a*) Estimated by means of Eq. (*3*). (*b*) Calculated from K_0 . x_B is the mole fraction of butadiene monomeric units. Data points (*cf.* Table I) for butadiene–styrene ○, butadiene–acrylonitrile ●. Lines calculated according to Eq. (*8*) with $C_A^\infty = 10{\cdot}9$ and $C_B^\infty = 5{\cdot}8$ (line *1*) and with $C_A^\infty = 7{\cdot}0$ aod $C_B^\infty = 5{\cdot}8$ (line 2). For details see text

In Fig. 4 the dependence on composition for "ideal" copolymers is represented by line 1 calculated by means of Eq. (8). The characteristic ratio for polybutadiene chains produced entirely by the 1,4 addition with all double bonds in the *trans* configuration is $C_B^\infty = 5.8$; for an all-*cis* chain, it is lower by 20% ($C_B^\infty = 4.8$ (refs[20–23]). The values for stereoirregular chains containing both types of double bonds in comparable amounts lie between these limits[24].

In copolymers discussed in this paper the ratio of *trans* to *cis* double bonds is approximately[11] 5 : 1 (SBR) and 6 : 1 (ABR) so that an appropriate value of C_B^∞ should be 5·6 or 5·7. The copolymers also contain vinyl side groups produced by the 1,2 addition of butadiene for which a higher (but unknown) C_B^∞ value is to be expected[24]. The proportion of 1,4 and 1,2 addition is usually 6 : 1 (SBR) and 10 : 1 (ABR) (ref.[11]). Regarding these facts, we consider the value $C_B^\infty = 5.8$ as adequate for inserting into Eq. (8).

The value $C_A^\infty = 10.9$ for polystyrene seems to be well established[1,25]. The situation is less easy with polyacrylonitrile as illustrated by the following values of C_A^∞: 9·1 (ref.[26]), 9·9 (ref.[27]), 12 (ref.[28]), and 13·8 (ref.[29]). The unusually broad range is probably due to difficulties of the experimental work with polyacrylonitrile solutions[30], to solvent effects on $\overline{R_0^2}/M$ (ref.[26]), and to the evaluation of K_0 from the $[\eta]$-values measured in good or mixed solvents. We do not prefer either of these values, and use the mean value ($C_A^\infty \simeq 11$) which is, perhaps incidentally, almost identical with that of polystyrene. This fact simplifies the discussion but the conclusions would remain qualitatively unchanged even if the extreme values were used.

The C^∞-values for the SBR copolymers are close to, or slightly below, the calculated line 1 (Fig. 4) and indicate that there exists no significant extra repulsive interaction within the styrene–butadiene dyads or that the rotation of a styrene unit is less hindered by an adjacent butadiene unit than by another styrene group. This

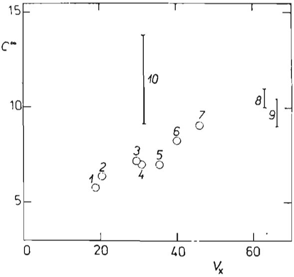

FIG. 5

Correlation of the characteristic ratio C^∞ for homopolymers with the molar volume (V_x) of the chain-repeating unit CH_2—CHX: *1* Polybutadiene[20–23] (abscissa equal $V_x/2$), *2* polyethylene[1], *3* poly(vinyl chloride)[33], *4* polypropylene[1] (atactic), *5* polyacrylic acid[1], *6* polyacrylamide[34], *7* poly(vinyl acetate)[1], *8* polystyrene[1,25], *9* poly(isopropyl acrylate)[1] (atactic), *10* polyacrylonitrile[26–29]. Values of C^∞ are not corrected for temperature effects is consistent with the actual knowledge of short-range interactions in the polystyrene and polybutadiene chains.

The high value of C_A^∞ for polystyrene is connected with strong steric repulsions due to the size of the phenyl group. On the other hand, theoretical calculations and experimental data[20-23,31] consistently show that rotations about the CH_2—CH_2 bonds in the polybutadiene chain are independent of the rotational states of the adjacent bonds and, consequently, free.

Before discussing the C^∞ values for ABR, let us consider Fig. 5. It represents a correlation of the characteristic ratio of several vinyl homopolymers with the molar volume V_x of the chain constitutional unit [*e.g.* CH_2—$CH(C_6H_5)$] calculated from the van der Waals group volumes[32]. The correlation is surprisingly good, only the data for polyacrylonitrile lie much above it. By its V_x value, polyacrylonitrile is comparable to polypropylene but its C_A^∞ value is close to that of polystyrene. Krigbaum and Tokita[35] have shown theoretically that the repulsive dipole–dipole interactions of adjacent nitrile groups are much more relevant for the configuration of the polyacrylonitrile chain than steric repulsions and are, therefore, responsible for the extended conformation of essentially atactic polyacrylonitrile chains.

The interaction of dipoles decreases with a high power of their distance. So, if acrylonitrile is copolymerized with a non-polar diene monomer in the proportion 1 : 1, the distance between dipoles becomes three times larger than in the polyacrylonitrile chain so that the repulsive interactions and their impact on the chain configuration are dramatically reduced. Under such conditions, the characteristic ratio for polypropylene would be a better reference value than that for polyacrylonitrile (at least at a high content of butadiene units). An „ideal" dependence of C^∞ on x_B calculated with $C_A^\infty = 7.0$ (for atactic polypropylene[1]) is drawn as a dotted line in Fig. 4.

We can see that while deviations of experimental points from line 1 are strongly negative over the whole span covered by the data, the deviations from line 2 are only slightly negative or even zero at $x_B \geq 0.5$. These facts indicate the absence of relevant dipole–dipole interactions at $x_B > 0.5$ and an increase in the rotational freedom of acrylonitrile monomeric units due to the adjacent butadiene units.

The situation is not clear at $x_B \leq 0.5$ but the position of the points for $x_B = 0.445$ may be assigned to the onset of dipole–dipole interactions. Nevertheless, measurements with copolymers at $x_B < 0.4$ would be very useful.

There are few copolymers known for which negative deviations from Eq. (*8*) have been found by experiments though, as indicated by theoretical calculations[17], they should be less exceptional than they seem to be. Statistical copolymers of butadiene with acrylonitrile and styrene are an example of such copolymers. The present paper shows that, if the theoretical analysis of configurational properties is too involved, experimental studies are meaningful provided their results can be confronted with those for similar substances whose configuration is well known.

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