data on samples 5 and 6. Similar shifts are observed in the polystyrene dispersions of two-phase block polymers of styrene with butadiene[8] and may be due to partial compatibility of the phases at these high temperatures. Such an effect would, of course, not be predictable by the mechanical equivalent model. It has, however, no bearing on the filler–rubber interaction at lower temperatures and would obviously not be present in elastomers reinforced with carbon black and other conventional fillers.

Conclusions

The dynamic behavior observed for polystyrene reinforced SBR is typical of other rubber-filled systems as well.[3] It can be described in all its essential features by a series–parallel coupled equivalent model. Thus it is not necessary to invoke an effect of the filler on the segmental motion of the rubber to explain the dynamic behavior. Since nuclear magnetic resonance and volume expansion measurements do not reveal a *substantial* effect of this nature, it must be concluded that the broadening of the relaxation spectrum of the *composite* is due primarily to other causes. The success of the equivalent model suggests that it may arise simply from mechanical coupling between the phases. Admittedly, the model is not a theory and only furnishes a phenomenological description. It is of interest, however, that theoretical stress analyses of rigid inclusions in viscoelastic media predict a broadening of the dispersion zone, even if the inclusions are perfectly elastic.[12]

Acknowledgment. The authors are indebted to C. A. Uraneck and J. E. Burleigh for the preparation of the polystyrene latex.

(12) J. R. M. Radok and C. L. Tai, *J. Appl. Polym. Sci.*, **6**, 518 (1962).

Notes

Huggins Constant k_Θ' for Chain Polymers at the Theta Point

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The Huggins constant k' in the expression for the viscosity η of dilute solutions of nonelectrolytic chain polymers has been studied by many investigators over

$$\eta = \eta_0(1 + [\eta]C + k'[\eta]^2C^2 + \ldots) \qquad (1)$$

the years.[1,2] Experiments show that near and in particular below the Θ point k' depends critically on the solvent power.[3,4] This characteristic, among others, has made unequivocal determination of k_Θ' for chain polymers at the Θ point rather difficult. Moreover, as pointed out in a previous work,[5] theories for k_Θ' differ markedly, and there has been no generally accepted value for k_Θ'. The above facts, in turn, suggest that once k_Θ' is established it may become a very sensitive criterion for the Θ point; that is, it may be possible to use k' in estimating the Θ point.

We present in this note some additional remarks which favor our previous estimate of k_Θ'. The present models for chain polymers under the Θ condition are freely interpenetrable spheres and hydrodynamically equivalent ellipsoids which are rigid and isolated. Although the models are quite different, values predicted for k_Θ' from either of them show good agreement.

In a previous work,[5] we have set bounds for k_Θ' on the basis of k' for the equivalent particles and also obtained the value $k_\Theta' = 0.523$ from the refined Peterson–Fixman theory. The latter theory uses soft spheres,[6] which become freely permeable under the Θ condition. From a different approach, but without noting that the model they employed corresponds closely to polymers at the Θ point, Weissberg and Prager have obtained the lower bound on the relative viscosity η/η_0 for suspensions of freely interpenetrable spheres.[7] Their results are

$$\eta/\eta_0 > 1/(1 - \phi)[1 - (3/2)\ln(1 - \phi)] \qquad (2a)$$

$$= 1 + 2.5\phi + 3.25\phi^2 + \ldots \qquad (2b)$$

where ϕ denotes volume fraction of the suspended spheres. Replacing 2.5ϕ with $[\eta]C$, we have

$$\eta/\eta_0 > 1 + [\eta]C + 0.520[\eta]^2C^2 + \ldots \qquad (3)$$

We may, therefore, postulate that the lower bound for k_Θ' should be

$$k_\Theta' > 0.520 \qquad (4)$$

Thus, the value $k_\Theta' = 0.523$ which was obtained without the use of a parametric pair distribution for interpenetrating polymer molecules, in contrast to the minimum k' calculated from the extended Peterson–Fixman theory for polymers in good solvents,[5] is seen to be very close to the lower bound.

Polymers at the Θ point should remain constant in size independently of concentration due to the absence

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(1) H. L. Frisch and R. Simha in "Rheology, Theory and Applications," Vol. I, F. R. Eirich, Ed., Academic Press, New York, N. Y., 1956, Chapter 14.

(2) W. R. Moore in "Progress in Polymer Science," Vol. I, A. D. Jenkins, Ed., Pergamon Press, Oxford, 1967, p 1.

(3) H. Inagaki, H. Suzuki, M. Fujii, and T. Matsuo, *J. Phys. Chem.*, **70**, 1718 (1966).

(4) T. A. Orofino, *J. Polym. Sci., Part A-2*, **6**, 575 (1968).

(5) T. Sakai, *ibid., Part A-2*, **6**, 1535 (1968).

(6) J. M. Peterson and M. Fixman, *J. Chem. Phys.*, **39**, 2516 (1963).

(7) H. L. Weissberg and S. Prager, *Trans. Soc. Rheol.*, **9** (**1**), 321 (1965).

of osmotic compression, and in this regard they may be treated as hard particles. For rigid particles of arbitrary shape, the Brinkman[8] and Roscoe[9] theory gives

$$k' = (1 + V_e/[\eta])/2 \tag{5a}$$

$$= (1 + 1/f_\eta(p))/2 \tag{5b}$$

where V_e is the hydrodynamic specific volume of the particles, and $f_\eta(p)$ represents a shape factor in the expression $[\eta] = f_\eta(p)V_e$. The shape factor is given by[10]

$$f_\eta(p) = 2.5 + 0.4075(p - 1)^{1.508} \qquad 1 \leq p < 15 \tag{6}$$

for prolate ellipsoids of the axial ratio p. The axial ratio p_Θ for ellipsoids which are equivalent to the polymers at the Θ point has been calculated by Gotlib and Svetlov[11] to be $p_\Theta > 3$ with pertinent regard to the stiffness of molecular chains. Therefore, bounds for the k_Θ' calculated from equivalent ellipsoids should be

$$0.5 < k_\Theta' < 0.637 \tag{7}$$

which embrace the lower bound, inequality 4, and our estimate $k_\Theta' = 0.523$. Additionally, the axial ratio p_Θ estimated from the Scheraga–Mandelkern–Flory[12] constant $\Phi^{1/3}P^{-1}$ and recent experiments[13,14] ($2.34 < \Phi_\Theta^{1/3}P_\Theta^{-1} \times 10^{-6} < 2.56$) falls in the range

$$7.3 < p_\Theta < 15.5 \tag{8}$$

from which, with eq 5b and 6, we have

$$0.52 < k_\Theta' < 0.56 \tag{9}$$

as the semiempirical bounds for k_Θ'. It may be interesting to note that these bounds are consistent with the theoretical bounds, inequalities 4 and 7.

Summarizing the above, for polymers of large enough molecular weight, to which the equivalent spheres of uniform segment density would apply better, we may conclude that

$$k_\Theta' \simeq 0.52 \tag{10}$$

This is in reasonable agreement with recent experiments,[14,15] although some other data show the change of k_Θ' with specific polymer–solvent interactions even for the cases of the Θ systems.[16] The effect of molecular weight of polymers and the specific interactions with solvents may diversify the unique value of k_Θ'. However, the semiempirical bounds of inequality 9 should be useful in the treatment of viscosity data at or near the Θ point. An even more interesting possibility is to invert the process and use experimental values of k' as criteria for locating the Θ condition. The investigation of this latter possibility will require very careful treatment of the experimental data.[17] Theoretical calculations based more directly on the random-flight chain model[18] will also be very pertinent in this connection.

(8) H. C. Brinkman, *J. Chem. Phys.*, **20**, 571 (1952).
(9) R. Roscoe, *Brit. J. Appl. Phys.*, **3**, 267 (1952).
(10) W. Kuhn, H. Kuhn, and P. Buchner, *Ergeb. Exakt. Naturw.*, **25**, 1 (1951).
(11) Yu. Ya. Gotlib and Yu. E. Svetlov, *Vysokomol. Soedin.*, **9**, 1150 (1967).
(12) H. A. Scheraga and L. Mandelkern, *J. Amer. Chem. Soc.*, **75**, 179 (1953). L. Mandelkern and P. J. Flory, *J. Chem. Phys.*, **20**, 212 (1952).
(13) J. M. G. Cowie and E. L. Cussler, *J. Chem. Phys.* **46**, 4886 (1967).
(14) M. Abe, K. Sakato, T. Kageyama, M. Fukatsu, and M. Kurata, *Bull. Chem. Soc., Jap.*, **41**, 2330 (1968).
(15) G. C. Berry, *J. Chem. Phys.*, **46**, 1338 (1967).
(16) T. A. Orofino and J. W. Mickey, Jr., *ibid.*, **38**, 2512 (1963); T. A. Orofino and A. Ciferri, *J. Phys. Chem.*, **68**, 3136 (1964).
(17) T. Sakai, *J. Polym. Sci., Part A-2*, **6**, 1659 (1968).
(18) S. Imai, *Proc. Roy. Soc.* (London), **A308**, 497 (1969).

Unit Cell of the Pseudomonoclinic Crystalline Component in Polyethylene

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A question was raised[1] as to whether our pseudomonoclinic unit cell, as published in ref 2, is a subcell or a full unit cell.

The cell, as shown in Figure 8 of the earlier publication, is exactly equal to one-fourth of the full unit cell shown here in Figure 1. This unit cell is consistent with the full translational symmetry of the lattice. Moreover, with adjacent reentry, the molecular folds conform fully with this symmetry. The lattice parameters of the full unit cell, and the *new hkl* indices for the *same* experimental and calculated *d spacings* reported in the earlier publication in Table I, are shown here in Table I. The *a* and *b* axes of the full unit cell are exactly twice the *a* and *b* axes of the subcell, the volume is four times larger, and there are four monomer units per unit cell.

The usual crystallographic convention for monoclinic cells (in which *b* is the unique axis and *β* the nonorthogonal angle) is set aside deliberately in order to facilitate comparison with the undistorted orthorhombic unit cell of polyethylene.

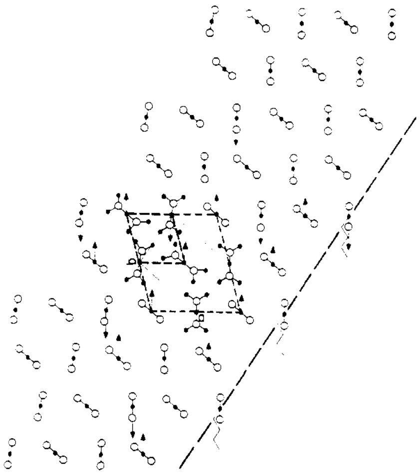

Figure 1. Schematic representation of a skewed lattice array in a lamellar ribbon of polyethylene.

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[1] The authors are grateful to Professor S. Krimm for bringing this aspect to our attention.

TABLE I
X-RAY DIFFRACTION RESULTS FOR THE ORTHORHOMBIC AND THE DERIVED PSEUDOMONOCLINIC UNIT CELLS OF TRANSCRYSTALLINE POLYETHYLENE

	Unit cell parameters		
Orthorhombic[a]	Derived pseudomonoclinic		
		Mono 1	Mono 2
a = 7.36 Å	a axis, Å	8.46	7.11
b = 4.92 Å	b axis, Å	9.44	5.46
c = 2.534 Å	c axis, Å	2.534	2.534
	γ angle, °	105.0	96.5
Volume 91.76 Å	Volume, Å^3	195.48	97.75
Monomer units in cell = 2	Monomer units in cell	4	2

Cu Kα radiation = 1.5406 Å

d spacing, Å units				*hkl*		
Ortho	Mono	Obsd	Intensity	Ortho	Mono 1	Mono 2
	4.559[b]	4.56	M–S		020	$\bar{1}10$
4.090	4.086	4.09	VVS	110	200	110
3.680		3.68	VS	200		
	3.531[c]	3.53	VW		$\bar{2}20$	200
2.947		2.95	W	210		
	2.714[d]	2.71	VVW		220	020
2.460		2.46	S	020		
2.333		2.33	VW	120		
2.253		2.25	W–S	011		
2.196		2.19	VVW	310		
2.154	2.154	2.15	W	111	201	111
2.087	2.076[b]	2.08–2.09	M	201 split	$4\bar{2}0$	310
2.045	2.043	2.04	W	220	400	220
1.921		1.92	VW	211		
1.840		1.85	VVW	400		
1.763				301		
1.737				320		
1.723				410		
1.716		1.71	M	121		
1.659		1.66	W	311		

[a] The parameters of the orthorhombic unit cell were taken from E. R. Walter and F. P. Reding, *J. Polym. Sci.*, **21**, 561 (1956). [b] Appears in all samples. [c] Appears in stretched samples. [d] Appears in unstretched samples.

A different possible full unit cell can also be considered on the *same lattice array*. This cell, as shown by lightly dashed lines in Figure 1, is also consistent with the full translational symmetry of the lattice array and with the adjacent reentry of molecular folds. It accounts very well for all observed "extra" reflections (see Table I) and the agreement between the experimentally measured and calculated d spacings using the derived lattice parameters is excellent. Consideration of the geometry of this cell suggests that the cell is, in effect, a distorted orthorhombic unit cell of polyethylene. This distortion could arise from slightly different polymer chain packing in a skewed lattice array during the growth of folded-chain lamellae as discussed at some length in our earlier publication.[2] The distortion of the orthorhombic unit cell to this skewed lattice array would involve a small decrease in the length of its a axis, a significant increase in the length of its b axis, and an increase in the γ angle to 96.5°, as is shown in Table I (mono 2). By convention, the smallest full unit cell must be consistent with the full translational symmetry of the lattice. Because this one is consistent, we therefore propose that this cell is the most probable one.

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Poly(hexamethylphosphoramide) and Its Copolymers

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The remarkable properties of hexamethylphosphoramide (HMPA), particularly its ability to dissociate ion pairs into free ions and to dissolve and ionize alkali metals, prompted us to synthesize a polymer of similar structure. This was accomplished by condensing piperazine with dimethylphosphoramidic dichloride ($OPCl_2N(CH_3)_2$) into

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[2] C. Gieniewski and R. S. Moore, *Macromolecules*, **2**, 385 1969).