Assignment of the decreased rate of growth observed in the present work, to one or more of these parameters would however be very difficult in the case of PEGA since each type of spherulite can only be studied in a narrow temperature range and so many parameters have to be determined as a function of *MW* and crosslinking density.

ACKNOWLEDGEMENTS

We thank Professor H. Berghmans of the University of Louvain for helpful discussions.

REFERENCES

1 Geuskens, G. in 'Comprehensive Chemical Kinetics', (Eds. C. H. Bamford and C. F. H. Tipper), Elsevier, Amsterdam, 1975, Vol 14
2 Point, J. J. *Bull. Acad. Roy. Belg.* 1955, **41**, 982
3 Takayanagi, M. and Yamashita, T. *J. Polym. Sci.* 1956, **22**, 552
4 Teitelbaum, B. Ya., Palikhov, N. A., Maklakov, L. I., Anoshina, N. P., Murtazina, I. O. and Kovalenko, V. I. *Vysokomol. Soedin. (A)* 1967, **9**, 1672
5 McCaffery, E. M. 'Laboratory Preparation for Macromolecular Chemistry', McGraw Hill, New York, 1970, p 57
6 David, C. in 'Comprehensive Chemical Kinetics', (Eds C. H. Bamford and C. F. H. Tipper), Elsevier, Amsterdam, 1975
7 Turnbull, D. and Fisher, J. C. *J. Chem. Phys.* 1949, **17**, 71
8 Lauritzen, J. I. and Hoffmann, J. D. *J. Appl. Phys.* 1973, **44**, 4340
9 Hoffmann, J. D., Frolen, L. J., Pross, G. S. and Lauritzen, J. I. *J. Res. Nat. Bur. Stand (A)* 1975, **79**, 671
10 Hoffmann, J. D. and Weeks, J. J. *J. Chem. Phys.* 1962, **37**, 1723
11 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
12 Kargin, V. and Slonimsky, G. L. 'Encyclopedia of Polymer Science', Interscience, New York, 1968, Vol. 8, p 445
13 Mandelkern, L. 'Crystallization of Polymers', McGraw Hill, New York, 1964

Solution properties and chain flexibility of poly(2-chlorophenyl methacrylate)

J. Niezette
Laboratoire de Chimie-Physique, Université de Liège, Sart-Tilman, B-4000 Liege, Belgium

and N. Hadjichristidis
Department of Industrial Chemistry, University of Athens, 13a Navarinou Street, Athens (144), Greece

(Received 27 July 1976; revised 6 September 1976)

As a part of our investigation programme about poly(methacrylic esters), we present here some results obtained for poly(2-chlorophenyl methacrylate) which are compared with those found for poly(phenyl methacrylate)[1] and other poly(chlorophenyl methacrylates)[2,3] in order to test the effect of the hydrogen–chlorine substitution on the solution properties and the chain flexibility.

Nine fractions of $\bar{M}_w$ from 6.7 x 10^4 to 74 x 10^4 were prepared and characterized in the way already described for other poly(methacrylic esters)[1,4]. Mark–Houwink constants, interaction parameters B of Stockmayer–Fixman relation, K_θ value and chain flexibility factor σ derived from viscosity measurements are collected in *Table 1*. The average value of K_θ corrected for polydispersity was obtained as previously[5] using the extrapolation methods proposed by Stockmayer–Fixman, Kurata–Stockmayer, Cowie, Kamide–Moore and Inagaki–Kurata. Adopting for the Flory constant ϕ the value of 2.87 x 10^{21}, we found the relation between the unperturbed dimension and molecular weight as:

$$\langle \bar{r}_0^2 \rangle^{1/2} = 0.50M^{1/2}(\text{Å})$$

The flexibility factor σ was calculated taking a freely rotating chain dimension $\langle \bar{r}_{0f}^2 \rangle^{1/2}$ of $0.22M^{1/2}$. The reported value is relatively low for a poly (methacrylic ester) having an aromatic side chain[5].

The preceding constants can be compared in *Table 1* with the corresponding values found for poly(phenyl methacrylate) and other poly(chlorophenyl methacrylates). More accurate σ values than those previously report-

Table 1 Mark–Houwink constants, interaction parameter B of Stockmayer–Fixman relation, K_θ average value and chain flexibility factor σ for poly(phenyl methacrylate) and poly(chlorophenyl methacrylates)

	Mark–Houwink constants				
Polymer–solvent	$K_a \times 10^3$ (cm^3/g)	a	$B \times 10^{28}$ (cm^3 g^{-2} mol^2)	$K_\theta \times 10^3$ (cm^3/g)	σ
Poly(2-chlorophenyl methacrylate):					
Tetrahydrofuran	3.2	0.74	–		
Dioxane	8.3	0.64	2.2	36	2.27
Benzene	9.33	0.62_5	1.5		
Toluene	41.9	0.45	–		
Poly(phenyl methacrylate)[1]:					
Dioxane	5.42	0.73	7.8	59	2.46
Benzene	5.75	0.72	6.4		
Poly(4-chlorophenyl methacrylate)[2]:					
Dioxane	6.1	0.70	3.45	48	2.50
Benzene	9.2	0.66	2.70		
Poly(2,4,5-trichlorophenyl methacrylate)[3]:					
Dioxane	11.8	0.58	1.0	26	2.37
Benzene	21.2	0.51_5	~0.0		

ed[1,2] were however proposed using a better polydispersity corrective factor[5]. It can be seen that halogen substitutions in the aromatic ring decrease the polymer–solvent interactions. Similar trends were observed in chloro-substituted polystyrenes[6]. The comparison between the σ factors show a specific effect of the *ortho*-substituent: as already discussed[3], poly (2, 4, 5-trichlorophenyl methacrylate) has a more flexible chain than poly (phenyl methacrylate) in spite of the three chlorine atoms attached to the aromatic ring but the contrast between the behaviour of poly(4-chlorophenyl methacrylate) and that of poly(2-chlorophenyl methacrylate) indicates clearly that only the chlorine atom in *ortho*-position tends to increase the flexibility. A quite similar conclusion can be drawn by comparing poly(2-t-butylphenyl methacrylate) ($\sigma = 2.40$)[7] with poly(4-t-butylphenyl methacrylate) ($\sigma = 2.57$)[8] but in this case the differences are less marked. Undoubtedly for poly(2-chlorophenyl methacrylate) a steric contribution of the chlorine atom in *ortho*-position cannot be considered alone since the effect of the very bulky t-butyl substituent appears to be less important. Additional contributions are very likely such as repulsive forces between C=O and C–Cl dipoles and also resonance effects which are particularly high in nuclear substituted phenyl methacrylates as shown by Otsu *et al.*[9]. It is reasonable to think that the combined actions of these factors can modify the configuration of the side groups to such an extent that the chain flexibility is increased.

REFERENCES

1 Hadjichristidis, N., Devaleriola, M. and Desreux, V. *Eur. Polym. J.* 1972, **8**, 1193
2 Tricot, M. and Desreux, V. *Makromol. Chem.* 1971, **149**, 185
3 Hadjichristidis, N. to be published
4 Sumrell, G., Campbell, P. G., Ham, G. E. and Schramm, C. H. *J. Am. Chem. Soc.* 1959, **81**, 4310
5 Niezette, J., Hadjichristidis, N. and Desreux, V. *Makromol. Chem.* 1976, **177**, 2069
6 Brandrup, J. and Immergut, E. M. 'Polymer Handbook', 2nd Edn, Wiley, New York, 1975
7 Tricot, M., Bleus, J. P., Riga, J. P. and Desreux, V. *Makromol. Chem.* 1974, **175**, 913
8 Gargallo, L. to be published
9 Otsu, T., Ito, T. and Imoto, M. *J. Polym. Sci. (A-1)* 1966, 733

Effect of chain length and branching on the interaction energies of polymer molecules

Rajeev Goel, Anil Kumar and Santosh K. Gupta
Department of Chemical Engineering, Indian Institute of Technology, Kanpur-208016, India
(Received 26 July 1976)

One of the approaches in the study of the excluded volume effect in polymer science is the modified Flory theory[1]. Results of this theory have been found to be in better agreement with experiments compared to other theories. In this theory, one requires the potential energy of interaction, $V(S)$, for a polymer molecule having a fixed radius of gyration, S. Results on $V(S)$ are available in the literature for linear chains having a large number of statistical segments[1,2]. In this work, $V(S)$ has been obtained for small chain lengths for linear as well as branched molecules.

FORMULATION

A polymer molecule is modelled as a sequence of n independent statistical segments, each having a mean square length, l^2. The time-averaged segment density at position r from the centre of mass has been obtained exactly for a molecule having any branched architecture as[3–5]:

$$\rho^0(r) = \frac{1}{\pi^{3/2}} \sum_{j=1}^{n} c_j^3 \exp(-c_j^2 r^2) \quad (1)$$

where c_j is given by:

$$c_j^2 = \frac{gn(n+2)}{4(n+1)\,\langle S^2\rangle_{0b} \sum_{i=1}^{n} v_{ji}^2} \equiv \frac{c_j^{*2}}{\langle S^2\rangle_{0b}} \quad (2)$$

$\langle S^2\rangle_{0,b}$ is the mean square radius of gyration of the chain, v_{ji} are the elements of a matrix V which depends on the molecular architecture of the chain[3–5] and g is the ratio of $\langle S^2\rangle_{0,b}$ to the mean square radius of gyration of a linear chain having the same number of statistical segments:

$$g = \langle S^2\rangle_{0,b} / \langle S^2\rangle_{0,\text{linear}} \quad (3)$$

g is known analytically[6,7] for common branched polymers.

Fixman[1,8] has shown that the potential energy of interaction, $V(S)$, for a polymer molecule having a radius of gyration S is given by:

$$\frac{V(S)}{kT} = \frac{\beta^*}{2} \int \rho^{0^2}(\mathbf{r}, S)\mathrm{d}\mathbf{r} \quad (4)$$

where k is the Boltzmann constant, T the absolute temperature and β^* the binary cluster integral characterizing the potential energy of interaction, V_{ij}, between the ith and jth statistical segments:

$$\beta^* = \int [1\{-\exp - V_{ij}(\mathbf{r}_{ij})/kT\}]\,\mathrm{d}\mathbf{r}_{ij} \quad (5)$$

In equation (4), $\rho^0(\mathbf{r}, S)$ is the averaged segment density for a chain having a radius of gyration S and is different from the segment density $\rho^0(r)$ which is the value without the latter constraint.

As it is extremely difficult to obtain $\rho^0(\mathbf{r}, S)$ numerically[1], one approximates it by $\rho^0(r)$ with S^2 substituted for $\langle S^2\rangle_{0b}$ in equations (1) and (2) to give:

$$\rho^0(\mathbf{r}, S) \simeq \frac{1}{\pi^{3/2}} \sum_{j=1}^{n} D_j^3 \exp(-D_j^2 r^2) \quad (6)$$

where

$$D_j^2 = \frac{c_j^{*2}}{S^2} \quad (7)$$

This approximation is completely analogous to that made by Flory[9]. Equations (4), (6) and (7) give finally: