

ed<sup>1,2</sup> were however proposed using a better polydispersity corrective factor<sup>5</sup>. It can be seen that halogen substitutions in the aromatic ring decrease the polymer-solvent interactions. Similar trends were observed in chloro-substituted polystyrenes<sup>6</sup>. The comparison between the  $\sigma$  factors show a specific effect of the *ortho*-substituent: as already discussed<sup>3</sup>, 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) ( $\sigma = 2.40$ )<sup>7</sup> with poly(4-t-butylphenyl methacrylate) ( $\sigma = 2.57$ )<sup>8</sup> 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.*<sup>9</sup>. 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 flex-

ibility 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

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(Received 26 July 1976)

One of the approaches in the study of the excluded volume effect in polymer science is the modified Flory theory<sup>1</sup>. 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<sup>1,2</sup>. 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<sup>3-5</sup>:

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

where  $c_j$  is given by:

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

$\langle S^2 \rangle_{0b}$  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<sup>3-5</sup> and  $g$  is the ratio of  $\langle S^2 \rangle_{0b}$  to the mean square radius of gyration of a linear chain having the same number of statistical segments:

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

$g$  is known analytically<sup>6,7</sup> for common branched polymers.

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

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

where  $k$  is the Boltzmann constant,  $T$  the absolute temperature and  $\beta^*$  the

binary cluster integral characterizing the potential energy of interaction,  $V_{ij}$ , between the  $i$ th and  $j$ th statistical segments:

$$\beta^* = \int [1 - \exp - V_{ij}(r_{ij})/kT] dr_{ij} \quad (5)$$

In equation (4),  $\rho^0(r, S)$  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  $\rho^0(r, S)$  numerically<sup>1</sup>, one approximates it by  $\rho^0(r)$  with  $S^2$  substituted for  $\langle S^2 \rangle_{0b}$  in equations (1) and (2) to give:

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

where

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

This approximation is completely analogous to that made by Flory<sup>9</sup>. Equations (4), (6) and (7) give finally:

$$\frac{V(S)}{kT} = \frac{\beta^*}{2S^3} \frac{1}{\pi^{3/2}} \times \sum_{j=1}^n \sum_{i=1}^n \frac{c_i^{*3} c_j^{*3}}{(c_i^{*2} + c_j^{*2})^{3/2}} \quad (8)$$

Since the total number of pairwise interactions in a molecule is  $n(n+1)/2$ , equation (8) may be written alternatively as:

$$\frac{V(S)}{kT} = \frac{n(n+1)\beta^*}{2S^3} \phi \quad (9)$$

where:

$$\phi = \frac{1}{n(n+1)\pi^{3/2}} \sum_{i=1}^n \sum_{j=1}^n \frac{c_j^{*3} c_i^{*3}}{[c_j^{*2} + c_i^{*2}]^{3/2}} \quad (10)$$

Equation (10) can be solved for polymer chains having different architecture and  $n$ , and their effects on the potential energy of interaction can be studied.

## RESULTS AND DISCUSSION

The quantity  $\phi$  characterizing the potential energy of interaction,  $V(S)$ , has been evaluated numerically for linear chains as well as for a 3-branch regular comb chain shown in Figure 1 for different values of  $n$ . The results are shown in Table 1. The number of segments required for asymptotic results to be applicable is found to de-

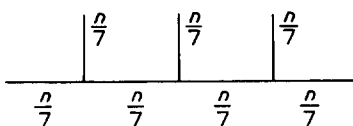


Figure 1 A three-branch regular comb chain

pend on the molecular architecture of the chain. For linear chains, the asymptotic value of  $\phi$ , 0.1416, is identical to that calculated by Casassa and Orofino<sup>2</sup>.

The effect of molecular architecture on the asymptotic value of  $\phi$  is shown in Table 2 in which results for several uniform star chains are presented. It is observed that  $\phi$  increases with the degree of branching. This is expected physically because, for the same value of  $S$ , a more highly branched chain would have a greater density of segments near the centre of mass, leading to higher interaction energies.

The calculated values of  $\phi$  and  $V(S)/kT$  can be used in the Boltzmann factor along with the distribution of the radius of gyration,  $W^0(S)$ , to study the excluded volume problem. It may be pointed out that since  $V(S)$  occurs in the exponential term, small changes in the value of  $\phi$  may lead to significant variations in the expansion factor,  $\alpha_S$ .

## CONCLUSIONS

In this work, it has been found that the attainment of the asymptote is postponed to higher values of  $n$  in branched chains. Also, the interaction energies are found to increase with the degree of branching, as expected physically. These are expected to have a significant influence in the computation of the expansion factor.

Table 1  $\phi$  for different values of  $n$  for linear and three-branched regular comb chains

Linear		3-branch regular comb	
$n$	$\phi$	$n$	$\phi$
4	0.1340	7	0.1361
8	0.1399	14	0.1399
12	0.1410	21	0.1408
16	0.1414	28	0.1412
20	0.1415	56	0.1417
40	0.1416	91	0.14185
60	0.1416	98	0.141865
80	0.1416		
100	0.1416		

Table 2  $\phi$  for a  $p$  branch regular star chain for large values of  $n$

$p$	$n$	$\phi$
3	99	0.1545
4	100	0.1623
5	100	0.1670
7	98	0.17095
10	200	0.1796

## REFERENCES

- 1 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971
- 2 Casassa, E. F. and Orofino, T. A. *J. Polym. Sci.* 1959, 35, 553
- 3 Gupta, S. K., Kumar, A. and Forsman, W. C. *Chem. Phys. Lett.* 1976, 39, 291
- 4 Goel, R., Kumar, A. and Gupta, S. K. *Chem. Phys. Lett.* 1976, 40, 45
- 5 Debye, P. and Bueche, F. J. *Chem. Phys.* 1952, 20, 1337
- 6 Zimm, B. H. and Stockmayer, W. H. *J. Chem. Phys.* 1949, 17, 1301
- 7 Forsman, W. C. *Macromolecules* 1968, 1, 343
- 8 Fixman, M. *J. Chem. Phys.* 1955, 23, 1656
- 9 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953