15 Nguyen, H. X., Amdur, S., Ehrlich, P. E. and Allendoerfer, R. D. *J. Polym. Sci. Polym. Symp.* 1978, **65**, 63
16 Tsonis, C. P. and Farona, M. F. *J. Polym. Sci. Polym. Chem. Edn.* 1979, **17**, 1779
17 Voronkov, M. G., Pukhnarevich, V. B., Sushchinskaya, S. P., Annenkova, V. Z., Annenkova, V. M. and Andreeva, N. J. *J. Polym. Sci. Polym. Chem. Edn.* 1980, **18**, 53
18 Katz, T. J. and Lee, S. J. *J. Am. Chem. Soc.* 1980, **102**, 422
19 Chippendale, J. C., Gil, P. C. and Warhurst, E. *Trans. Faraday Soc.* 1967, **63**, 1088
20 Pople, J. A. and Beveridge, D. L. 'Approximate Molecular Orbital Theory', McGraw-Hill, New York, 1970
21 Sipe, Jr., H. J., Kispert, L. D., Hwang, J. S. and Tsonis, C. P., in press

The dipole moment of poly-*p*-chlorostyrene

Noriko Yamaguchi, Mari Sato, Etsuyo Ogawa and Mikiko Shima
Tokyo Woman's Christian University, Zempukuji, Suginami-ku, Tokyo 167, *Japan*
(*Received* 12 *July* 1981)

Introduction

The dipole moment of a polar polymer is related to the orientation of the monomer units. The observed dipole moment is the statistical average of the molecular conformation. Since the mean-squared dipole moment of a chain in which the dipole moment is perpendicular to the main chain axis should not be affected by long range interaction, *i.e.* excluded volume effect[1], dielectric constant measurement is favorable for characterizing the molecular conformations.

In this communication, we report on the dipole moment of poly-*p*-chlorostyrene (PClSt) measured in cumene over a wide range of temperatures.

Experimental

The anionic polymerization of *p*-chlorostyrene was carried out in THF at $-78°C$ under 10^{-6} mm Hg with Na-α-methylstyrene tetramer used as the initiator. The polymer obtained was dissolved in benzene, reprecipitated with methanol and dried in vacuum to a constant weight.

Determination of the intrinsic viscosity in cumene indicated its molecular weight which amounted to 6.7×10^4. Approximately the same value was obtained from the g.p.c. measurement of the molecular weight with toluene used as the eluent.

The dipole moment per monomer unit was determined by measuring the dielectric constant and the density of the cumene solutions of PClSt of several concentrations from 2 to 6% over a temperature range from 25° to 65°C. The cell was composed of coaxial platinum cylinders enclosed in a glass tube. The capacitance was measured by the heterodyne beat method at 500 kHz. Calibration of the apparatus was carried out by using purified benzene at each temperature measurement.

The specific polarization, p_2, of the polymer at infinite dilution was calculated according to the Halverstadt–Kumler equations[2].

$$p_2 = p_1\left(1 + \frac{3\alpha}{(\varepsilon_1 - 1)(\varepsilon_1 + 2)} - \frac{\beta}{d_1}\right), \; p_1 = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\cdot\frac{1}{d_1},$$

$$\alpha = \{(\varepsilon_{12} - \varepsilon_1)/w\}_{av} \text{ and } \beta = \{(d_{12} - d_1)/w\}_{av}$$

0032–3861/81/111464–02$02.00

where, w is the weight fraction of polymer, ε is the dielectric constant and d is the density. The suffixes 1, 2 and 12 refer to solvent, solute and solution, respectively. The dipole moment per monomer unit, μ, was calculated by following equation;

$$\mu = \{9kT(P_2 - (MR)_D)/4\pi N\}^{1/2}$$

where, P_2 is the molecular polarization of a monomer unit in the polymer and is given by p_2 multiplied by the molecular weight of the monomer unit, $(MR)_D$ is the molecular refraction of the monomer unit, k is the Boltzmann constant, N is the Avogadro's number and T is the absolute temperature.

Results and Discussion

The experimental results are listed in *Table 1*. Cumene is a θ-solvent for PClSt ($\theta = 59.0°C$)[3]. Our previous study[4] on the PClSt sample of molecular weight 3.8×10^5 in cumene showed that precipitation occured when the temperature of the solution decreased to several degrees below 59°C. The solution of the present sample, however, was soluble far below the θ-temperature and remained clear even at 40°C, partly because of its lower molecular weight compared with that of the previous sample. On lowering the temperature to approximately 30°C, the solution became translucent, but no precipitation was observed over several hours.

In *Figure 1*, the values of α and β plotted against temperature, respectively, show that there is no conspicuous trend suggestive of any influence of intra- and

Table 1 Dielectric polarization and dipole moment of poly-*p*-chlorostyrene in cumene

Temperature (°C)	α	β	p_2	P_2 (cc.)	μ(D)
25.0	1.697	0.2941	0.5512	76.39	1.36_6
30.0	1.640	0.2909	0.5445	75.46	1.36_0
40.0	1.591	0.2964	0.5375	74.49	1.36_4
50.0	1.483	0.2893	0.5242	72.64	1.35_0
55.0	1.448	0.2913	0.5185	71.85	1.34_4
65.0	1.344	0.2931	0.5011	69.45	1.31_6

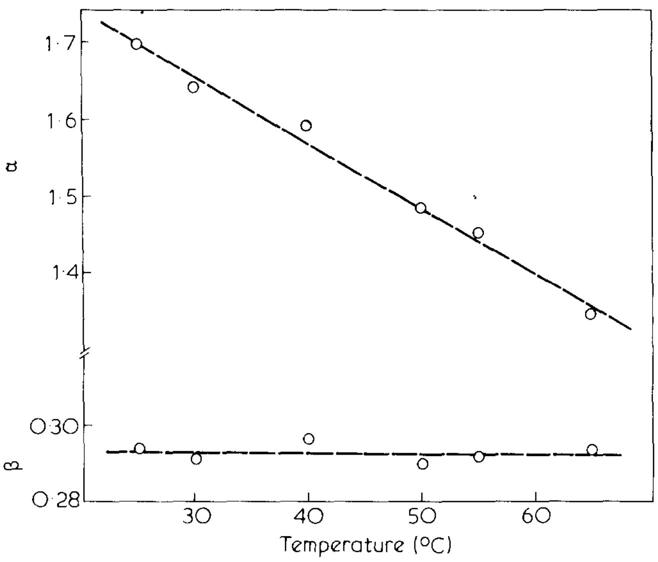

Figure 1 Temperature dependence of parameters α and β for poly-*p*-chlorostyrene in cumene

inter-molecular association. Therefore, the dipole moment calculated from α and β values is worthy of further discussion.

The value of μ, 1.36 D, in cumene at 30°C agrees with the previous result, 1.35 D, obtained for PClSt ($M_w = 5.1 \times 10^5$) in toluene at 30°C[5]. The agreement of the values seems to support the generally accepted theory that the excluded volume has little influence on the dipole moment of the polymer.

As shown in *Figure 2*, the dipole moment decreased with the increase in temperature. The temperature coefficient of the mean-square dipole moment, $d\ln\langle\mu^2\rangle/dT$, was calculated to be -1.6×10^{-3} by the least-square method.

The values obtained for μ in this study are within the range of the published values, 1.24∼1.60 D [6–8]. The temperature coefficient, $d\ln\langle\mu^2\rangle/dT$, obtained, is somewhat smaller than the reported value[7], -4×10^{-3}. However, the present experimental results for μ and the temperature coefficient are in agreement with those calculated for the atactic stereochemical structure using a rotational isomeric state model[9,10].

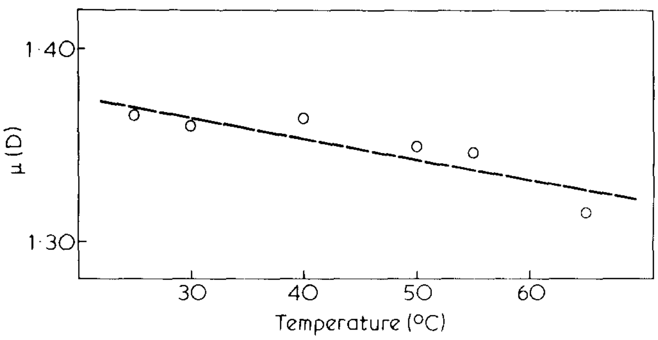

Figure 2 Temperature dependence of the dipole moment for poly-*p*-chlorostyrene in cumene

References

1 Stockmayer, W. H. *Pure Appl. Chem.* 1967, **15**, 539
2 Halverstadt, I. F. and Kumler, W. D. *J. Am. Chem. Soc.* 1942, **64**, 2988
3 Izumi, Y. and Miyake, Y. *Polym. J.* 1973, **4**, 205
4 Shima, M., Ogawa, E. and Sato, M. *Polymer* 1979, **20**, 311
5 Shima, M., Yamaguchi, N., Ogawa, E. and Sato, M. *Reports on Grants for Fundamental Research in Chemistry* 1979, 47
6 Debye, P. and Bueche, F. *J. Chem. Phys.* 1951, **19**, 589
7 Burshtein, L. L. and Stepanova, T. P. *Polym. Sci. USSR* 1969, **11**, 2885
8 Baysal, B., Lowry, B. A., Yu, H. and Stockmayer, W. H. in 'Dielectric Properties of Polymers', edited by F. E. Karasz, Plenum, New York, 1972
9 Mark, J. E. *J. Chem. Phys.* 1972, **56**, 458
10 Saiz, E., Mark, J. E. and Flory, P. J. *Macromolecules* 1977, **10**, 967