into account. The exact chain conformation, however, is under study and will be published after the final analysis of the present X-ray fiber diffraction study.

No X-ray study has been reported on (1→4)-α-D-galactan, but it would be expected to take a similar conformation to that of the present poly[galactosamine] if substituting the hydroxyl group for the amino group at C(2) does not affect the 2_1 symmetry: for example, in the case of glucopyranosyl polysaccharides, both cellulose and chitosan show 2_1 symmetry. On the other hand, substituting the carboxyl group for the hydroxymethyl at C(5) may change the conformation from 2_1 to 3_1[2-5] symmetry. Our recent conformational analysis for (1→4)-α-D-galactan[17] suggested that the galactan was able to take a twofold helical structure with a fiber repeat of 8.7 Å though the energetically most favorable conformation was a 2_1 helix having a 8.9-Å fiber repeat and that a threefold helix with a 13.5-Å fiber repeat was possible as well.

It is important to discuss the conformational difference between (1→4)-linked glucopyranose and galactopyranose polymers. Amylose, the α-D-glucan, forms a large-amplitude 6-fold helix. According to our previous conformational analysis, the energetically most stable structure of β-D-galactan is an expanded 6-fold helix.[18] On the other hand, the present poly[α-D-galactosamine] (and maybe the α-D-galactan) and common cellulose, the β-D-glucan, take ribbonlike structures, although the latter is nearly fully extended and the former is kinked. Pectic acid, poly[α-D-galacturonic acid], takes a threefold helix, but it has an h value (4.43 Å), the rise per residue along the helix axis, similar to that of the present poly[galactosamine] (h = 4.35 Å), indicating that they do not have any drastic conformational difference.

Acknowledgment. We are grateful to Professors A. Sarko and P. Zugenmaier for the use of PS 79 program.

References and Notes

(1) Ogawa, K.; Hirano, S.; Miyanishi, T.; Yui, T.; Watanabe, T. *Macromolecules* **1984**, *17*, 973.
(2) Palmer, K. J.; Hartzog, M. B. *J. Am. Chem. Soc.* **1945**, *67*, 2122.
(3) Palmer, K. J.; Merrill, R. C.; Owens, H. S.; Ballantyne, M. *J. Phys. Colloid Chem.* **1947**, *51*, 710.
(4) Walkinshaw, M. D.; Arnott, S. *J. Mol. Biol.* **1981**, *153*, 1055.
(5) Walkinshaw, M. D.; Arnott, S. *J. Mol. Biol.* **1981**, *153*, 1075.
(6) Takagi, H.; Kadowaki, K. *Agric. Biol. Chem.* **1985**, *49*, 3151.
(7) Takagi, H.; Kadowaki, K. *Agric. Biol. Chem.* **1985**, *49*, 3159.
(8) The use of a glass beaker made it difficult to remove the resultant fiber since the fiber adhered strongly to the glass.
(9) Less than 5-min immersion did not give a stable fiber while 10-min standing caused loss of fiber orientation.
(10) The fiber before annealing gave a diffuse pattern having only one equatorial reflection (d = 6.4 Å) when X-rayed at 100% relative humidity. Under vacuum a much more diffuse pattern was observed. These indicate a different polymorph, including water molecules from that of the annealed material.
(11) Palmer, K. J.; Ballantyne, M. *J. Am. Chem. Soc.* **1950**, *72*, 736.
(12) Morris, E. R.; Powell, D. A.; Gidley, M. J.; Rees, D. A. *J. Mol. Biol.* **1982**, *155*, 507.
(13) Atkins, E. D. T.; Nieduszynski, I. A.; Mackie, W.; Parker, K. D.; Smolko, E. E. *Biopolymers* **1973**, *12*, 1879.
(14) Sarko, A.; Zugenmaier, P. FORTRAN Virtual Bond Refinement Program PS 79.
(15) Zugenmaier, P.; Sarko, A. In *Fiber Diffraction Methods*; A. D., French, K. H., Gardner, Eds; American Chemical Society: Washington, D.C., 1980; *ACS Symp. Ser. No. 141*, p 225.
(16) Sheldrick, B. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 1016.
(17) Tanaka, F.; Ogawa, K.; Mizoguchi, Y.; Shutoh, Y.; Okamura, K.; Koshijima, T. *Wood Res. Techn. Notes* **1986**, *No. 22*, 46.
(18) Tanaka, F.; Mizoguchi Y.; Shutoh, Y.; Okamura, K.; Ogawa, K.; Koshijima, T. *Wood Res. Techn. Notes* **1986**, *No. 22*, 37.

Kozo Ogawa*

Radiation Center of Osaka Prefecture
Shinke-cho, Sakai, Osaka 593, Japan

Fumio Tanaka

Wood Research Institute
Kyoto University
Uji, Kyoto 611, Japan

Jun-ichi Tamura and Kiyoshi Kadowaki

Research Laboratory
Higeta Shoyu Co., Ltd.
Choshi-shi, Chiba 288, Japan

Keizo Okamura

Department of Wood Science and Technology
Faculty of Agriculture, Kyoto University
Kyoto 606, Japan

Received January 13, 1987

Correlation between the Glass Transition Temperatures of Polymer Mixtures and Intermolecular Force Parameters

In a previous publication[1] an equation of the following form was proposed to account for the variation of the glass transition temperatures of mixtures of poly(methyl methacrylate) (PMMA) and phenolic resins with blend compositions.

$$T_g = (W_1T_{g1} + kW_2T_{g2})/(W_1 + kW_2) + qW_1W_2 \quad (1)$$

The first term on the right-hand side of eq 1 is identical with the widely used Gordon–Taylor[2] expression, and the second term represents the effect of polymer–polymer interaction, hydrogen bonding for the blends under consideration, on T_g. Note that eq 1 reduces to an earlier equation by Jenckel and Heusch[3] when k = 1. But experimental T_g data for several mixtures can be fitted only by k values not equal to unity. Equation 1 is also different from the one used by Tsutsui et al.,[4] in which the second term is $qW_1W_2/(W_1 + kW_2)$.

Additional reports appeared recently on the use of eq 1 to represent the T_g data of polymer mixtures. Of particular interest are the results of Percec and co-workers[5,6] on blends of polymers containing electron donor and acceptor groups, for which the values of q were found to be positive in some mixtures but negative in others. Almost simultaneously Pennacchia et al.[7] also found that the T_g data for mixtures of PMMA with p-NO_2- or p-t-Bu-substituted phenolic resins could be represented by eq 1 with negative q values.

Originally, it was thought that interchain specific interaction, at least in the case of hydrogen bonding, reduced segment mobility and raised T_g in a way analogous to cross-linking and q could be regarded as a measure of such

Table I
q and k Values from T_g Data

	PMMA		PEMA	
substituent	q	k	q	k
p-hydro	44.2	0.89	42.2	1
p-methyl	41.2	0.88	44.0	1
p-*tert*-butyl	−39.4	1	−38.8	1
p-nitro	−41.9	1	−54.7	1
p-fluoro	67.9	0.87	68.2	0.89
p-chloro	44.8	1	52.4	1

0024-9297/87/2220-1174$01.50/0

Table II
Contributions of Each Independent Variable to q

X	$L\sigma_{lX}$	$D\sigma_{dX}$	$A_{\alpha X}$	q_x obsd PMMA	q_x obsd PEMA	q_x calcd	Δ^a PMMA	Δ^a PEMA
H	0	0	0	44.2	42.2	45.3	-1.1	-3.1
Me	0.503	17.8	-24.6	41.2	44.0	39.0	2.2	5.0
t-Bu	0.503	19.1	-99.3	-39.4	-38.8	-34.5	-4.9	-3.8
NO_2	-33.7	-22.9	-33.6	-41.9	-54.7	-44.9	3.0	9.8
F	-27.2	61.0	0.53	67.9	68.2	79.6	-11.7	-11.4
Cl	-23.6	35.6	-26.7	44.8	52.4	30.6	14.2	21.8

[a] $\Delta = q_{x,obsd} - q_{x,calcd}$.

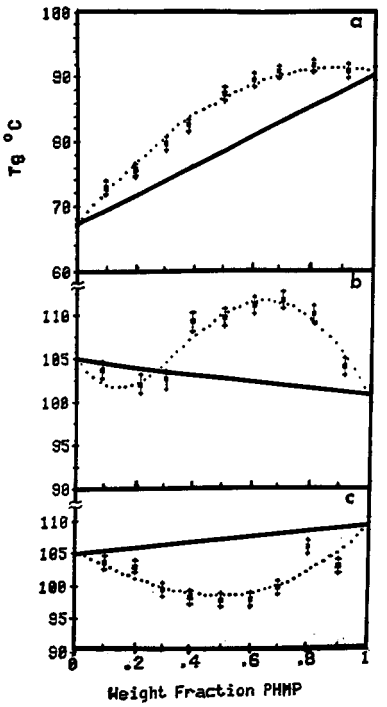

Figure 1. Glass transition temperatures of PHMP blends (a) *p*-H PHMP and PEMA, $k = 1$, $q = 42.2$, (b) *p*-F PHMP and PMMA, $k = 0.87$, $q = 67.9$, and (c) *p*-*t*-Bu PHMP and PMMA, $k = 1$, $q = -39.4$. Data (■); values calculated by eq 1 (···).

a contribution. In that context q would be expected to be always positive. That the values of q can also be negative calls for a reexamination of the original premise. Therefore we have expanded our earlier work on blends of PMMA and phenolic resins to include poly(ethyl methacrylate) and five para substituted phenolic resins with ortho–ortho methylene linkages, poly[(1-hydroxy-2,6-phenylene)-methylenes], or *o,o*-PHMPs. The para substituents are methyl, *tert*-butyl, nitro, fluoro, and chloro groups. (The synthesis of these *o,o*-PHMPs has been described in ref 7). Together with the *p*-H group of the unsubstituted resin, the groups cover a range of electronic and steric contributions, and it is our hope that the experimental data from these blends may provide a better insight to the nature of q, based on considerations of intermolecular force parameters.

The T_g data of these blends can all be fitted by eq 1. The calculated k and q values are listed in Table I. Typical curves for (a) a positive value of q, $k = 1$, (b) a positive value of q, $k \neq 1$, and (c) a negative value of q, $k = 1$ are shown in Figure 1.

In the following, we attempt to correlate the variation of q with polymer structure by the use of the intermolecular force (IMF) equation which may be written

$$q = L\sigma_l + D\sigma_d + R\sigma_e + S\nu + A\alpha + H_2N_n + B_{meth}p_{meth} + q_0$$

In the above equation, σ_l, σ_d, σ_e, ν, and α are substituent constants for localized, delocalized, electronic demand, steric, and polarization effects, respectively, and q_0 is the intercept of the linear equation. The parameter N_n is a hydrogen bonding parameter related to the number of lone pairs of electrons on an oxygen or nitrogen atom; this term is included because both PHMP–PHMP and PHMP–PMMA hydrogen bonding interactions are important. As the repeating units of the two methacrylate polymers differ only by a methylene group, we have combined the two sets of data into a single set by means of the indicator variable p_{meth}, which takes the value of unity for PEMA mixtures and zero for PMMA mixtures. The IMF constants are readily available from extensive compilations by Charton,[8,9] and the polarizability parameters are derived from the group molar refractivities reported by Hansch and Leo.[10]

For the six groups studied, α and ν are strongly collinear (zeroth-order partial correlation coefficient $r_{\alpha\nu} = 0.948$), σ_d and σ_e are collinear ($r_{de} = 0.832$) and N_n is collinear in σ_l, σ_d, and σ_e ($r_{ln} = 0.603$, $r_{dn} = 0.702$, and $r_{en} = 0.722$). Furthermore, the p_{meth} term turns out to be insignificant. Accordingly, only three independent IMF constants are needed for correlation and the best correlation equation is

$$q = L\sigma_l + D\sigma_d + A\alpha + q_0$$

Where $L = -50.3 \pm 12.5$, $D = -127 \pm 16.9$, $A = -534 \pm 58.4$, and $q_0 = 45.3 \pm 7.06$. The statistics obtained from the regression analysis are reported as follows: $100R^2$, the percent of the variance of the data accounted for by the correlation equation; F, a measure of the goodness of the fit; S, the standard error of the estimate; S^0, the standard error of the estimate divided by the root mean square of the data, also used as a measure of the goodness of the fit. We obtain, for our calculation of 12 data points, $100R^2 = 95.40$, $F = 55.32$, $S = 11.9$, and $S^0 = 0.263$. By calculating the contributions of each independent variable to the value of q we can explain the negative q values obtained for the nitro and *tert*-butyl groups. These contributions are reported in Table II. In the case of the nitro group the negative sign of q is due to both electrical and steric/polarizability effects. In the case of the *tert*-butyl group the steric/polarizability effect alone is responsible. Again, it is necessary to keep in mind the high degree of collinearity between the polarizability and steric parameters which makes it uncertain as to whether the observed effect is due to polarizability, to steric effects, or to some combination of the two factors. The determination of the q value for 4-trifluoromethyl PHMP would help to differentiate the two contributions.

Acknowledgment. The work was supported in part by the National Science Foundation, Grant DMR-8303499.

Registry No. PMMA, 9011-14-7; PEMA, 9003-42-3; (C_6H_5OH)(HCHO) (copolymer), 9003-35-4; (4-MeC_6H_4OH)(HCHO) (copolymer), 25053-88-7; (4-*t*-BuC_6H_4OH)(HCHO) (copolymer),

25085-50-1; (4-$O_2NC_6H_4OH$)(HCHO) (copolymer), 27322-28-7; (4-FC_6H_4OH)(HCHO) (copolymer), 26045-02-3; (4-ClC_6H_4-OH)(HCHO) (copolymer), 26045-03-4.

References and Notes

(1) Kwei, T. K. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 307.
(2) Gordon, M.; Taylor, J. S. *J. Appl. Chem.* **1952**, 2, 495.
(3) Jenckel, E.; Heusch, R. *Kolloid Z.* **1953**, *30*, 89.
(4) Tsutsui, T.; Nakano, H.; Tanaka, R.; Tanaka, T. *Kobunshi Ronbunshu* **1978**, *35*, 517.
(5) Rodriguez-Parada, J. M.; Percec, V. *Macromolecules* **1986**, *19*, 55.
(6) Pugh, C.; Percec, V. *Macromolecules* **1986**, *19*, 65.
(7) Pennacchia, J.; Pearce, E. M.; Kwei, T. K.; Bulkin, B. J.; Chen, J. P. *Macromolecules* **1986**, *19*, 973.
(8) Charton, M. *Prog. Phys. Org. Chem.*, in press.
(9) Charton, M. *Top. Curr. Chem.* **1983**, *57*, 114.
(10) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979.

T. K. Kwei,* Eli M. Pearce, John R. Pennacchia, and M. Charton

Polymer Research Institute
Polytechnic University
Brooklyn, New York 11201

Received January 20, 1987