generate the same polymer in the reversed direction. This asymmetry can be exhibited by third- and higher order Markov models; to each such model corresponds a reversed model which generates the same polymers in the reversed direction. Also, to each such model and to each n there corresponds a reversible Markov model which generates polymers having the same n-*ad* proportions, and that are statistically completely indistinguishable from their reversals. It seems desirable to to use only Markov models of this kind so long as observational data cannot distinguish the direction of chain growth.

The two-state Coleman-Fox model is not of finite Markov order, and the question arises as to whether it is reversible. We show below that it is, so that the polymers it generates are indistinguishable from their reversals. The model involves the parameters λ_a, λ_b, $k_1 = k_{1i} + k_{1s}$, $k_2 = k_{2i} + k_{2s}$ mentioned above. It is very convenient to use vector and matrix algebra to express the properties of the model. We put

$$t = \lambda_a k_1 + \lambda_b k_2$$
$$d = t + k_1 k_2$$

and define the 2 × 2 matrices

$$U_m = \begin{pmatrix} k_{1i}/k_1 & 0 \\ 0 & k_{2i}/k_2 \end{pmatrix} \qquad U_r = \begin{pmatrix} k_{1s}/k_1 & 0 \\ 0 & k_{2s}/k_2 \end{pmatrix}$$

$$D = \begin{pmatrix} 1 - \lambda_a k_1/d & \lambda_b k_2/d \\ \lambda_a k_1/d & 1 - \lambda_b k_2/d \end{pmatrix} \qquad T = \begin{pmatrix} \lambda_a k_1/t & 0 \\ 0 & \lambda_b k_2/t \end{pmatrix}$$

For any $n + 1$-*ad*, $q = q_1 q_2 \ldots q_n$ (where each q_j is either m or r) we define the 1 × 2 vector

$$V_q = [\text{Prob(chain ends in } q\text{, and is in state 1)}, \\ \text{Prob(chain ends in } q\text{, and is in state 2)}]$$

Under this model, the proportional frequency of q will be

$$[q] = \text{Prob(chain ends in } q) = V_q 1'$$

where 1 is the 1 × 2 vector (1,1) and (1′ is its transpose).

The power of this notation, using matrix multiplication, becomes clear when we observe that

$$\begin{aligned} V_{qm} &= V_q D U_m & V_{qr} &= V_q D U_r \\ V_m &= 1 T U_m & V_r &= 1 T U_r \end{aligned} \qquad \text{(A2-1)}$$

Now consider any $n + 1$-*ad*, $q_1 q_2 \ldots q_n$. From eq A2-1 we have

$$[q_1 q_2 \ldots q_n] = V_{q_1 q_2 \ldots q_n} 1' = 1 T U_1 D U_2 D U_3 \ldots D U_n 1' \qquad \text{(A2-2)}$$

where each U_j is U_m or U_r according as q_j is m or r. For the reversed $n + 1$-*ad* we have

$$[q_n q_{n-1} \ldots q_1] = 1 T U_n D U_{n-1} \ldots D U_1 1' \qquad \text{(A2-3)}$$

To show that these are equal, transpose eq A2-3 and use the facts that $U_m = U_m'$, $U_r = U_r'$, $TU_m = U_m T$, $TU_r = U_r T$, $TD = D'T$. This gives

$$\begin{aligned} \text{(A2-3)} &= 1 U_1 D' U_2 \ldots U_{n-1} D' U_n T 1' \\ &= 1 U_1 D' U_2 \ldots U_{n-1} D' T U_n 1' \\ &= 1 U_1 D' U_2 \ldots U_{n-1} T D U_n 1' \\ &= 1 U_1 T D U_2 \ldots U_{n-1} D U_n 1' \\ &= \text{(A2-2)} \end{aligned}$$

Thus $q_1 \ldots q_n$ and $q_n \ldots q_1$ are equally probable under the two-state Coleman-Fox model. However, the three-state version of the model will not be reversible, in general.

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The Influence of Stereoregularity on the Glass Transition Temperatures of Vinyl Polymers

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ABSTRACT: Correlation of available data for glass transition temperatures of mono- and disubstituted vinyl polymers, $(CH_2CXY)_n$, leads to the conclusion that steric configuration affects T_g only when $X \neq Y$ and neither X or Y is hydrogen. Conversely, T_g is independent of configuration when hydrogen is one of the substituents. A basis for this observation can be developed in terms of the Gibbs–DiMarzio theory if it is postulated that (a) the effect of configuration in disubstituted polymers is intramolecular and is brought about by changes in the flex energy of the isomers, and (b) changes in T_g due to side-chain modification are strictly intermolecular. Using the Simha–Boyer constant of 0.113 for the product $T_g \Delta\alpha$ (where $\Delta\alpha$ is the difference in the volume expansion coefficient above and below T_g), the unoccupied volumes at T_g and the flex energy differences for the syndiotactic and isotactic poly(methyl methacrylates) were calculated. The above postulates imply that the configuration-induced difference in T_g in the poly(alkyl methacrylates) should be constant. This appears to be approximately true, but cannot be properly verified as yet because the completely syndiotactic polymers have not been prepared.

Since the development of techniques for the synthesis of stereoregular vinyl polymers, there has been interest in studying the effect of steric configuration on the physical and mechanical properties of these substances. In the present paper we wish first to draw attention to some correlations of the effect of molecular structure and configuration on the glass transition temperatures, T_g, of certain classes of such polymers, second to provide a theoretical basis for these observations, and third to attempt quantitative predictions

TABLE I

EFFECT OF TACTICITY AND OF SIDE-CHAIN LENGTH ON T_g'S (°C) IN THE POLYMETHACRYLATE AND POLYACRYLATE SERIES

	—Methacrylates—			—Acrylates—	
R	Conventional[a]	Isotactic[c]	Δ	Conventional[c]	Isotactic
Methyl	105	43	62	8	10
Ethyl	65	8	57	−24	−25
Propyl	35			−44[b]	
Isopropyl	81[c]	27	54	−6	−11
Butyl	20	−24	44	−49[b]	
Isobutyl	53[c]	8	45	−24	
sec-Butyl	60[b]			−22	−23
Cyclohexyl	104[b]	51	53	19	12

[a] See S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61,** 985 (1957), unless otherwise noted. [b] O. G. Lewis, "Physical Constants of Linear Homopolymers," Springer-Verlag, New York, N. Y., 1968. [c] See ref 3.

of T_g's for as yet unprepared members of these classes.

Some Empirical Correlations. 1. In vinyl polymers of the type $(CH_2CXY)_n$, it has been noted[1] that T_g varies with tacticity only when neither of the two dissimilar substituents X and Y is hydrogen. The most extensive documentation of this effect is in the poly(alkyl methacrylate) series ($X = CH_3$, $Y = COOR$) in which it has been shown that the T_g's of the syndiotactic isomers exceed that of the isotactic isomers by as much as 80°.[2,3] Similarly, for poly-α-methylstyrene ($X = CH_3$, $Y = C_6H_5$), T_g(atactic) is 170°,[4] while T_g(isotactic) is 117°.[5] Appropriate data for other disubstituted polymers are still lacking.

Conversely, it can be demonstrated that in monosubstituted vinyl polymers ($X = H$), tacticity has essentially no effect on T_g. Examples are the poly(alkyl acrylate) series ($Y = COOR$),[3,6] polystyrene ($Y = C_6H_5$),[1] polypropylene ($Y = CH_3$),[7] and the higher poly-α-olefins ($Y = (CH_2)_nCH_3$).[8] Available data for the polymethacrylate and polyacrylate ester series are shown in Table I.

In certain cases, *e.g.*, poly(4-methylpentene-1), small differences in T_g for the different isomers have been reported,[9,10] but we believe these are due to the effects of crystallinity (of the isotactic polymers) rather than tacticity *per se*. It has also been reported that polyvinyl chloride ($X = H$, $Y = Cl$) is an exception to the rule stated above, inasmuch as the T_g of this polymer increases as the free-radical polymerization temperature decreases.[11] However, it was later shown that the tacticity of PVC is essentially unaffected by polymerization temperature[12,13] and the observed effects on T_g may in fact be due to variability in chain branching.

It should be obvious that in comparing T_g's of steric isomers it would be desirable to compare the 100% syndiotactic isomers with the corresponding 100% isotactic isomer. However, the former have apparently not been prepared. Conventional polymers, prepared by free-radical polymerization at ambient temperatures, are largely syndiotactic;[14] the syndiotacticity can be somewhat increased by lowering the reaction temperature. It is probable that the decrease in the T_g difference of conventional and isotactic methacrylates, with increasing side chain length (Table I), is due to a decrease in the syndiotacticity of the conventional polymers.

2. A second effect has been studied in the poly(alkyl acrylate) and poly(alkyl methacrylate) series. In "conventional" methacrylate polymers it is observed that T_g decreases monotonically with increasing side-chain length. A similar effect occurs in the poly(alkyl acrylates) (atactic and isotactic).[3,6] For isotactic methacrylates the effect is again encountered and also (as we have observed) the T_g of each isotactic member is lower than the T_g of the corresponding "conventional" polymer by an approximately constant amount. (With very long ester side chains, the T_g's start to increase again. This effect has been attributed to side-chain crystallization and will not be discussed further here.) These effects have been explained on the basis of "internal plasticization."[15] As the length of the ester side chain increases, neighboring chains are pushed further apart, increasing the free volume at a given temperature and decreasing the hindrance to chain backbone motions. Insofar as the glass transition can be considered to be at least approximately correlated with an iso-free-volume state,[16] this concept qualitatively explains the lowering of T_g. The important point is that the trends are similar for all the polymers in Table I, regardless of configuration, and that the effect therefore is primarily an intermolecular one.

Discussion

A basis for the effects summarized above can be developed in terms of the Gibbs-DiMarzio theory of the glass transition,[17] using the following two postulates.

1. The tacticity effect arises from the fact that, when neither substituent is hydrogen, the energy difference between the two predominant rotational isomers is greater for the syndiotactic configuration than for the isotactic configuration. However, when one of the substituents is hydrogen, the energy difference between the rotamers of the two configurations is the same.

2. The effect of increasing the ester side chain length in the poly(alkyl methacrylates) and poly(alkyl acryl-

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ates) is to modify intermolecular interactions, and to leave the intramolecular interactions unchanged.

Before proceeding, we first discuss T_g for 100% syndiotactic poly(methyl methacrylate). As already stated, this polymer has not been prepared, but there are two estimates of T_g in the literature. Mercier, Berghmans, and Smets[18] obtained a value of 148° by an extrapolation based on the Gordon–Taylor equation. Thompson[19] obtained a value of 160° by plotting T_g as a function of the fraction of syndiotactic diads as measured by nmr, and similarly extrapolating. In view of the uncertainties inherent in these approximations, the agreement is good. For our purposes we may reasonably take 160° as the T_g of totally syndiotactic PMMA.

In 1962, Simha and Boyer[20] proposed that the product $T_g\Delta\alpha$, where $\Delta\alpha$ is the difference in the volume expansion coefficient above and below T_g, should be a universal constant for all polymers. Using the data available to them then, Simha and Boyer found a range of values for this product which averaged to $T_g\Delta\alpha = 0.113$. A difficulty was encountered when this relationship was applied to the atactic poly(alkyl methacrylates) and poly(alkyl acrylates). It is known that the ester side group in these polymers relaxes independently of the main chain, a phenomenon arising from the hindered rotation of the ester side group about the C–C bond linking it to the main chain.[21] This relaxation occurs below the main glass transition and gives rise to a further change in the expansion coefficient. Simha and Boyer suggested that $\Delta\alpha$ should be calculated by using the coefficient of expansion above T_g and that below the temperature of the side-chain relaxation (about 35° in atactic PMMA). Recent results of Haldon and Simha[22] have confirmed the validity of this suggestion for several members of the methacrylate series produced by conventional polymerization.

It is now possible also to obtain a reliable value for $T_g\Delta\alpha$ for the isotactic poly(methyl methacrylate), using the T_g determination of Thompson and the recent $\Delta\alpha$ determination of Wittmann and Kovacs.[23] These authors measured the expansion coefficient for isotactic poly(methyl methacrylate) in the region below the side-chain relaxation as well as above the main glass transition. Their value for $\Delta\alpha$ is 3.64×10^{-4} cm^3 g^{-1} deg^{-1}. Using 48° for T_g leads to $T_g\Delta\alpha = 0.118$, essentially identical with the "universal" value of 0.113. This suggests therefore that the $T_g\Delta\alpha$ rule may be applicable to the methacrylates, regardless of tacticity, if the "correct," consistent values for $\Delta\alpha$ are taken. We note that this in turn supports an iso-free-volume concept since it has been shown,[24,25] on the basis of the Gibbs–DiMarzio theory, that

$$T_g\Delta\alpha = \frac{V_o \ln[(1+V_o)^2/4V_o]}{[2(1-V_o)/(1+V_o)] - [4V_o/(1+V_o)] \times \ln[(1+V_o)^2/4V_o] - [1-V_o]} \quad (1)$$

where V_o is the unoccupied volume at T_g, or actually at T_2.[17] $T_g\Delta\alpha$ is seen to be a function of V_o only and this constancy in the former quantity thus implies an iso-free-volume glass transition state.

From the experimental value for $T_g\Delta\alpha$ and eq 1 we find $V_o = 0.025$ at T_2, identical with the fractional free volume at the glass temperature obtained from the empirical WLF equation.[26] We have made the tacit assumption that there is a constant proportionality between the experimentally observed T_g and the Gibbs–DiMarzio T_2. Recent investigations support the contention that $T_2 \simeq 0.8T_g$ for a wide variety of glass-forming liquids,[27] and we have used this value in our calculation of V_o.

The hole formation energy, E_o, is also a function of V_o and T_g alone, since[17,25]

$$E_o = \frac{kT_g}{2}[(1+V_o)/(1-V_o)]^2 \ln[(1+V_o)^2/4V_o] \quad (2)$$

and thus for constant V_o, E_o is directly proportional to T_g. This has already been discussed by Eisenberg and Saito;[25] our proportionality constant (2.56) differs slightly from that of the latter investigators because of the lower V_o.

The calculation of the second parameter in the Gibbs–DiMarzio treatment, the "flex energy," ϵ, is similarly dependent only upon V_o.

$$-\ln[(1+V_o)/2] + (V_o/V_o - 1)\ln[(1+V_o)^2/4V_o] = \ln[1 + 2\exp(-\epsilon/kT_g)] + \frac{(2\epsilon/kT_g)\exp(-\epsilon/kT_g)}{1 + 2\exp(-\epsilon/kT_g)} \quad (3)$$

Using the result $V_o = 0.025$, we find $\epsilon/kT_g = 1.70$ and this then holds for any polymer obeying the universal Simha–Boyer relation.

Applying these considerations to poly(methyl methacrylate), we can obtain a numerical result for ϵ/k(syndiotactic) − ϵ/k(isotactic) since the T_g's are available for both configurational isomers. This value is $\Delta\epsilon/k = 191°$. By postulates 1 and 2, this result applies to any syndiotactic–isotactic poly(alkyl methacrylate) pair having the same ester side chains, and for any such pair T_g(syndiotactic) − T_g(isotactic) = 112°. More generally, for any syndiotactic–isotactic pair obeying the "universal" Simha–Boyer relationship

$$T_g(\text{syndiotactic}) - T_g(\text{isotactic}) = 0.59\,\Delta\epsilon/k \quad (4)$$

Table II shows calculated values for the T_g's of totally syndiotactic poly(alkyl methacrylates) based on available values of the T_g's of the isotactic isomers. Also included are the values of $\Delta\alpha$ calculated from the $T_g\Delta\alpha$ relationship. Where possible, literature values for $\Delta\alpha$ of the "conventional" polymers are cited. Owing to the paucity of the available data, uncertainties introduced by tacticity effects, and the effect of the side chain relaxation, it is difficult to compare theoretical and experimental $\Delta\alpha$'s.

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TABLE II
T_g's (°C) AND $\Delta\alpha$'s (°C^{-1}) FOR STEREOREGULAR POLY(ALKYL METHACRYLATES)

Polymer	T_g (syndio)[a]	T_g (iso)[b]	$10^4\Delta\alpha$ (syndio)[a]	$10^4\Delta\alpha$ (iso)[a]	$10^4\Delta\alpha$ (conventional)
Methyl	160	43	2.6	3.6	2.45, 3.05[d]
Ethyl	120	8	2.8	4.0	2.65,[d] 3.0[c]
Isopropyl	139	27	2.7	3.7	
Butyl	88	−24	3.0	4.4	2.3,[d] 3.4[c]
Isobutyl	120	8	2.8	3.9	2.4[d]
Cyclohexyl	163	51	2.6	3.5	

[a] Estimated, see text. [b] See ref 3. [c] See ref 22. [d] See ref 25.

It is tempting to propose that the same numerical relationship between the T_g's of the syndiotactic and isotactic isomers would also hold for the poly(2-chloroacrylates) inasmuch as the van der Waals radius of the chloride radical is very close to that of the methyl group. However, it is known that the T_g's of conventional 2-chloroacrylates are higher than those of conventional methacrylates.[28] This is probably due to the strong intermolecular forces introduced by the presence of the polar chloride groups. No data are as yet available concerning the effect of stereoregularity on the T_g's of the chloroacrylates, or of other 2-substituted acrylate polymers.

Finally, it is interesting to note that the constancy of $T_g\Delta\alpha$ in the methacrylates implies that the pressure dependence of T_g should not be a function of tacticity, at least in PMMA. This is because it has been experimentally shown that the change in heat capacity at T_g, ΔC_p is independent of tacticity[29] and thus, using the equation[30]

$$\frac{dT_g}{dP} \simeq \frac{T_g V \Delta\alpha}{\Delta C_p} \tag{5}$$

and the fact that the specific volumes at the respective T_g's are almost identical,[23] it follows that dT_g/dP is similarly independent.

Conclusions

1. This paper has drawn attention to the correlations that exist between the glass transition temperatures, steric configuration and side-chain structure in mono- and disubstituted vinyl polymers.
2. The Simha–Boyer universal values for $T_g\Delta\alpha$ appear to hold, regardless of tacticity, for PMMA, and this in turn implies constancy in V_o, the Gibbs–DiMarzio unoccupied volume, at T_g for these polymers.
3. If we assume that the effect of tacticity on T_g in the poly(alkyl methacrylate) series is strictly an intramolecular effect, then it may be shown that the differences in T_g (for totally syndio- and isotactic polymers) is constant for the series and may be predicted.
4. It is suggested that this analysis will hold for other disubstituted vinyl polymers, and that major differences in T_g should be found, for example, for the various tactic poly-2-chloroacrylates.

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Temperature and Stress Dependence of Creep in an Acrylonitrile–Butadiene–Styrene Polymer

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ABSTRACT: Tensile creep measurements were carried out on a commercial acrylonitrile–butadiene–styrene (ABS) polymer over a temperature range from 40 to 100° at stress levels from 0.6 to 1.8 × 10^8 dyn/cm^2. Experiments were conducted in a prototype of an apparatus designed to be compatible with digital acquisition systems. Analysis of the data indicated that application of the time–temperature superposition principle was of limited value due to the use of test temperatures near and below the effective glass transition temperature of the acrylonitrile–styrene component of the polymer. A strong stress dependence of the compliance was observed, even at relatively short times after loading. This was analyzed in terms of a model in which the height of the potential energy barrier to motion of the molecular flow unit is lowered by the application of stress. From this analysis the apparent volume of the flow unit was found to range from 8 to 13 Å^3 depending on the temperature and the time chosen for analysis. The slight time dependence indicated that at relatively short times the apparent size of the flow unit is smaller, but rapidly tends toward a somewhat larger asymptotic value. Analysis of the temperature dependence of the tensile viscosity and the temperature dependence of the stress required to produce a characteristic isochronal response indicated that the effective T_g of the acrylonitrile–styrene phase is about 85°. The stress dependence of the glass transition temperature is considered as well as the limitations involved in extrapolation of experimental data to long times and high stress levels.

Most analyses of the stress dependence of creep in acrylonitrile–butadiene–styrene (ABS) polymers have been carried out using empirical equations to describe the creep response. These suffer the disadvantage of not providing insight into the nature of the stress dependence, and, moreover, they usually