be obtained from experiment.

We have performed computer simulations on clusters of dipoles to determine which orientations of the dipoles minimize the electrostatic energy and hence to obtain the ground state ($T = 0$) energy of the cluster. Starting with a completely random distribution of orientations, we allow the dipoles to relax into a self-consistently stable arrangement. This ground state is highly degenerate as a consequence of the symmetry of the array, and so different initial conditions lead to various final orientations. Figure 1 shows a ground-state configuration for a cluster of 30 dipoles. Figure 2 is a plot of the electrostatic energy per dipole as a function of the number of dipoles in a cluster; typical values have been assumed for the parameters that enter our model. We see that the binding energy per dipole, E_{es}/N, initially increases with N and then reaches a constant value for $N \gtrsim 30$.

Most of the information needed in order to make qualitative predictions about T_g is contained in Figure 2. For example, if the average number of dipoles per cluster is known, we can obtain an estimate for $T_g^{cluster}$ from

$$-E_{es} = {}^3/_2 N k_B T_g^{cluster} \quad (2)$$

where k_B is Boltzmann's constant. We have argued earlier that $T_g^{cluster}$ can be identified with the glass transition temperature of the ionomer. Hence we will drop the superscript in $T_g^{cluster}$ and simply denote this quantity by T_g. The glass transition temperature could be determined more precisely by carrying out Monte Carlo simulations to study the behavior of thermodynamic quantities such as the specific heat as a function of temperature; for the present purposes, however, eq 2 will suffice since we are interested only in qualitative trends. We point out that eq 2 overestimates T_g since we have neglected the elastic contribution to the ground-state energy of the system. When dipoles aggregate to form clusters, the polymer chains to which the fixed ions are attached become deformed, and these conformational deformations give rise to an elastic energy that raises the ground-state energy of the system above that given by Figure 2. However, this contributes a constant term which we will ignore at this point since it does not qualitatively alter the behavior of our system.

We see from eq 2 that a plot of T_g as a function of N, the number of dipoles in the system, is simply the negative of the curve shown in Figure 2. This looks very similar to experimental plots[4] of T_g for Nafion-Cs as a function of Cs^+ content when the ionomer is neutralized from the acid form to the salt form. It is known that the degree of aggregation increases[2] as an ionomer is neutralized, and hence we believe that the mechanism in Figure 2 is responsible for the observed variation of T_g with increasing neutralization. We point out that the conventional explanation predicts $T_g \propto q/a$, where q is the charge of the counterion and a is the sum of the ionic radii of the ions that form a dipole. This leads, in contradiction with experiment, to a decrease in T_g as neutralization increases, since the charge of Cs^+ is the same as that of H^+ while the ionic radius of Cs^+ is larger than that of H^+. We also point out that our model predicts that the glass transition in an ionomer occurs over a broad temperature range, as is experimentally observed.[4] This is because in a real system we expect to find a distribution of clusters of different sizes, each of which "melts" at its own temperature.

This analysis also lends itself to a discussion of the effect of water absorption and counterion type on the glass transition temperature. Our model predicts that T_g decreases as water content increases, since water that is absorbed in the hydrophilic ionic regions causes the dielectric constant to increase, thereby reducing the electrostatic binding energy. Similarly, we would expect that T_g will decrease as counterion radius increases, because the dipole length a increases with counterion radius and it can be seen by a dimensional argument that $E_{es} \propto 1/a$. Both the above predictions appear to be consistent with experiment.

Acknowledgment. We thank A. J. Hopfinger for useful discussions. This work was supported by NSF Grant CPE81-151115.

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Received January 3, 1984

Group-Transfer Polymerization. 3. Lewis Acid Catalysis

Anionic polymerization of methacrylates is widely recognized as being capable of producing living polymers with controlled molecular weight and narrow molecular weight distribution (MWD). Simple alkyl acrylates, on the other hand, have been found[1] to behave quite differently from methacrylates in anionic polymerization, generally giving poor conversion, broad MWD, and loss of living ends so that block copolymer formation fails. We have chosen to address the problem of controlled polymerization of acrylates by the use of group-transfer polymerization (GTP). A recent report[2] has described the anion-catalyzed, ketene silyl acetal initiated polymerization of acrylic monomers. In this communication we describe the use of zinc halides and dialkylaluminum halides and oxides as Lewis acid catalysts for GTP and demonstrate their particular advantage in the preparation of polyacrylates of narrow MWD.

Zinc halides[3a-c] and dialkylaluminum chlorides[3d] have been widely used as catalysts for alkylations and other reactions of silyl enol ethers and ketene silyl acetals. We find that zinc chloride, bromide, and iodide and dialkylaluminum chlorides and oxides are effective catalysts for GTP of acrylates and methacrylates with initiation by the ketene silyl acetal (1, Scheme I). The resulting polyacrylates and -methacrylates have a narrow MWD, and the degree of polymerization is controlled by the ratio of monomer to initiator used (see Tables I and II). The MWD of polyacrylates prepared by GTP with the Lewis acid catalysts is generally narrower than that of polyacrylates prepared by GTP using anion catalysts such as

0024-9297/84/2217-1415$01.50/0

Table I
Zinc Halide Catalyzed Group-Transfer Polymerization[a]

entry	monomer	cat. (solvent)	initiator	theor. MW	GPC results $\bar{M}_n$	GPC results $\bar{M}_w$	GPC results D	% yield
1	**2**	$ZnBr_2$ (methylene chloride)	1		1600	2600	1.60	11
2	ethyl acrylate	ZnI_2 (methylene chloride)	4	3360	3300	3400	1.03	100
3	ethyl acrylate	ZnI_2 (ethylene dichloride)	4	1195	1250	1380	1.10	100
4	methyl methacrylate	$ZnBr_2$ (ethylene dichloride)	1	3400	6020	7240	1.20	100
5	ethyl acrylate	$ZnCl_2$ (toluene)	1	4100	5800	11300	1.96	100
6	ethyl acrylate	$ZnBr_2$ (ethylene dichloride)	1	10100	17000	26600	1.57	100

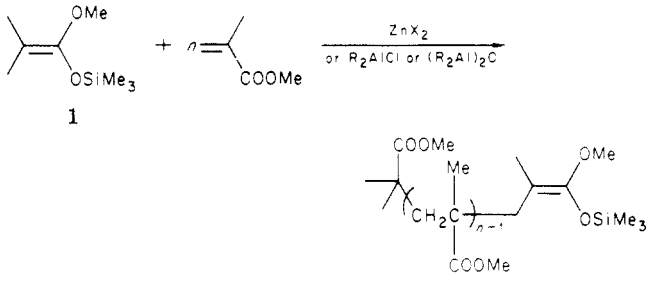
[a] For comparison, GTP of butyl acrylate in tetrahydrofuran solution at 0 °C using 1 as initiator and tris(dimethylamino)sulfonium bifluoride as catalyst gave quantitative conversion to polymer with $\bar{M}_n$ = 27 200, $\bar{M}_w$ = 59 400, and D = 2.16 (theoretical molecular weight 26 100).

Table II
Dialkylaluminum Chloride and Dialkylaluminum Oxide Catalyzed Group-Transfer Polymerization Initiated by 1

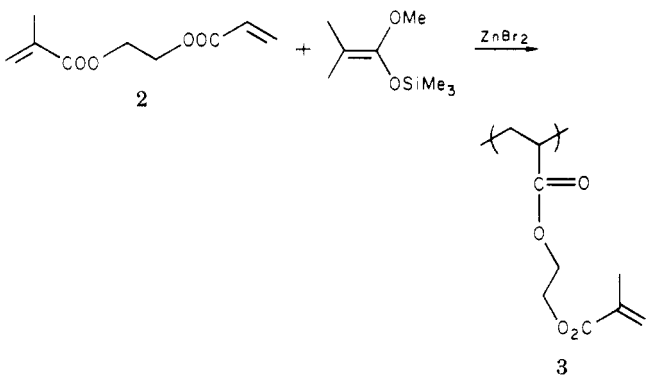
entry	monomer	cat. (solvent, T (°C))	cat. theor MW	GPC results $\bar{M}_n$	GPC results $\bar{M}_w$	GPC results D	% yield
1	ethyl acrylate	$(i\text{-}Bu_2Al)_2O$[a] (toluene, 20–58)	2100	1330	1580	1.19	100
2	methyl methacrylate	$i\text{-}Bu_2AlCl$ (methylene chloride, 25–30)	1465	3000	8500	2.43	21
3	butyl acrylate	$i\text{-}Bu_2AlCl$ (methylene chloride, −78)	2660	2370	2520	1.06	100
4	ethyl acrylate	$(i\text{-}Bu_2Al)_2O$[a] (2:1 acetonitrile–methylene chloride, −78)	2100	1980	2380	1.20	97
5	ethyl acrylate	Et_2AlCl (methylene chloride, −78)	2100	2340	2740	1.17	100

[a] Mixed oligomers prepared by the addition of 0.5 equiv of water to triisobutylaluminum in toluene solution.

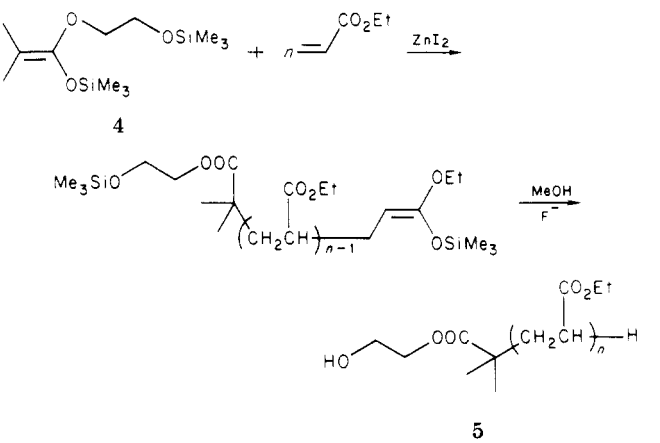
Scheme I



Scheme II



Scheme III



bifluoride ion[2] (see Table I, footnote *a*).

Donor solvents must be avoided in Lewis acid catalyzed GTP, with halogenated alkanes and aromatic hydrocarbons being the preferred solvents.[4,5] The aluminum catalysts, however, can also be used with acetonitrile as the principal solvent (Table II, entry 4). In contrast to anion-catalyzed GTP, in which 0.1 mol % (relative to initiator) bifluoride catalyst produces a high rate of polymerization, zinc halide catalysts should be present at levels of about 10–20 mol % relative to monomer to achieve complete conversions of acrylates and methacrylates, while the aluminum catalysts are generally used at 10–20 mol % initiator. The mode of catalysis of the Lewis acids appears to be coordination with the carbonyl oxygen atom of the monomer, thus activating the monomer toward nucleophilic attack by the ketene silyl acetal. The zinc halide catalysts perform best at ambient temperature, and molecular weight control is best with zinc iodide and poorest with zinc chloride (see Table I, entries 2 and 5). In the case of the aluminum catalysts, there is a competing decomposition reaction that leads to low conversions of methacrylates at ambient temperature and that permits good conversions of acrylates only in a batch process (addition of catalyst to solution of monomer and initiator) at ambient temperature. At −78 °C, however, the decomposition is suppressed, and acrylates are polymerized by a monomer feed process to give living polymer with good molecular weight control (Table II, entries 1, 2, and 4).

A useful method for generating anhydrous zinc bromide or zinc iodide in situ as a slurry in a halogenated alkane is the reaction of diethylzinc with 2 equiv of bromine or iodine.[6] The oligomeric dialkylaluminum oxides are prepared in situ by reaction of aluminum trialkyls with 0.5 equiv of water.[7]

Acrylates are much more reactive than methacrylates in Lewis acid catalyzed GTP. Thus, 2-(methacryloxy)ethyl acrylate (**2**) at low conversion yields a polyacrylate with pendant methacrylate groups (**3**; see Table I, entry 1, and Scheme II). ^1H NMR of the product shows the absence of unpolymerized acrylate, and only monomeric methacrylate is present. Polymerization of ethyl acrylate with a ketene silyl acetal initiator containing a trimethylsilyl-protected hydroxyl group,[8] **4**, in the presence of zinc iodide gave a quantitative yield of hydroxyl-terminated poly(ethyl acrylate) (**5**; see Table I, entries 2 and 3, and Scheme III).

Poly(methyl methacrylate) prepared with Lewis acid catalysts (at all temperatures) contains approximately twice as many syndiotactic as heterotactic sequences. This contrasts with the 1:1 syndiotactic:heterotactic ratio observed with bifluoride catalyst at ambient temperature but approximates the tacticity observed with bifluoride catalyst at −78 °C.[2] Poly(ethyl acrylate) prepared by GTP with anionic or Lewis acid catalysts has random tacticity.

Lewis acid catalyzed GTP of simple alkyl acrylates provides a powerful means for control of polymer architecture that far exceeds the results obtained with anionic polymerization.[1]

Acknowledgment. We are indebted to M. C. Han for gel permeation chromatographic measurements, R. C. Ferguson and D. W. Ovenall for ^1H and ^{13}C NMR studies, and Toni Anemone for preparation of the manuscript.

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(4) In a typical procedure, zinc iodide (6.48 g, 20 mmol) was heated in a 100-mL three-necked flask to 300 °C in vacuo for 30 min and then allowed to cool under argon. Then dichloromethane (50 mL) was added followed by 1-(trimethylsiloxy)-1-(2-(trimethylsiloxy)ethoxy)isobutene[8] (1.4 mL, 4.71 mmol). After the mixture was cooled to −78 °C, ethyl acrylate (10 mL, 92.22 mmol) was added. The reaction was allowed to warm to −15 °C, whereupon the temperature rose very quickly to +38 °C over 3 min. The temperature was allowed to fall to +20 °C. When more ethyl acrylate (1.0 mL, 0.92 mmol) was added, no further reaction occurred. The solvent was evaporated, and the residue was dissolved in ethyl acetate (100 mL) and washed three times with 100-mL portions of water. The organic layer was dried over $MgSO_4$, filtered, and evaporated to give 9.91 g of poly(ethyl acrylate). GPC: $\bar{M}_n$ = 2200, $\bar{M}_w$ = 2300, D = 1.05 (theoretical molecular weight 2160).
(5) In a typical procedure, a solution of 0.87 g (1 mL, 5 mmol) of 1-methoxy-1-(trimethylsiloxy)isobutene in 20 mL of anhydrous methylene chloride was cooled to −78 °C under an argon atmosphere and treated with 0.28 mL (0.5 mmol) of 1.8 M diethylaluminum chloride/toluene. Then 10 g (10.8 mL, 100 mmol) of ethyl acrylate (purified by passage over a short column of neutral alumina under an argon atmosphere) was added at such a rate that the temperature of the reaction mixture did not exceed −70 °C. After 15 min at −78 °C, 5 mL of methanol was added, and the mixture was allowed to warm to room temperature. Evaporation under reduced pressure gave 10.7 g of poly(ethyl acrylate) as a viscous liquid. GPC: $\bar{M}_n$ = 2130, $\bar{M}_w$ = 2580, D = 1.21 (theoretical molecular weight 2100).
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Received March 14, 1984

Depression of Glass Transition Temperature in Aramid–Polybutadiene Multiblock Copolymers

A number of studies on two-phase polymer systems have shown that the properties of a finely dispersed microphase are not the same as those of the polymer in bulk. The relation between glass transition temperature (T_g) and two-phase morphology is still unsolved.[1] Two-phase polymers that segregate into distinct large domains usually exhibit two T_g's identical with those of the component polymers. When the domains are very small, say less than a few hundred angstroms, the T_g's of the individual components are shifted: elevation of the temperature of the low T_g and depression of the high T_g. This inward shift of both T_g's has been observed by Meyer et al.[2] on styrene–isoprene–styrene block copolymers and by Gaur et al.[3] on high molecular weight block copolymers of α-methylstyrene and styrene. The depression of the high T_g of hard-component microphases dispersed in a soft matrix has been observed by many authors.[4] Bares[5] interpreted the high-T_g depression as the effect of an interfacial zone that increases the average free volume available to the glassy microphase. Couchman et al.[6] argued that even in the absence of the finite interfacial zone, the effect of interfacial tension on the equilibrium pressure within the microphase will cause the high-T_g depression.

On the other hand, the *depression* of the *low* Tg has been observed in rubber-toughened plastics such as ABS (acrylonitrile–butadiene–styrene copolymer), HIPS (high-impact polystyrene), and blends of styrene–butadiene block copolymer with the corresponding homopolymers.[7-9] These systems consist of microspherical inclusions of a rubber in a rigid plastic matrix. Depression of the rubber T_g has been explained on the basis of negative pressure resulting from differential contraction due to the thermal expansion mismatch upon cooling from the liquid state.[7-9]

Here we report another T_g shift phenomenon: the depression of the low T_g of a rubber matrix in aramid–polybutadiene multiblock copolymers.

We prepared a series of aramid–polybutadiene multiblock copolymers having various lengths of aramid and a constant length of polybutadiene. Direct polycondensation of isophthalic acid with excess 4,4′-diaminodiphenyl ether was carried out in *N*-methylpyrrolidone/LiCl with triphenyl phosphite/pyridine as the condensing agent. Block copolymerization of the oligoaramid with α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ = 5200) was performed in the same way. The multiblock copolymer is poly(4,4′-oxydi-*p*-phenyleneisophthalamide)-*b*-polybutadiene (Figure 1). Details of the polymer synthesis will be presented elsewhere.[10] The block copolymer was dissolved in DMAc (*N*,*N*′-dimethylacetamide) and the solution was cast onto a flat dish. The solvent was evaporated at room temperature under reduced pressure for 60 h.[11] Prior to further drying, the cast film was washed with methanol in a Soxhlet extractor for 0.5 h to exchange any residual solvent in the film with methanol. Finally, the film was dried under a vacuum of 10^{-4} mmHg at 80 °C for 1 day. The film thus prepared was used for differential scanning calorimetry (DSC) and electron microscopy.

DSC thermograms were obtained at a constant heating rate of 20 °C/min. For transmission electron microscopy, osmium tetraoxide staining and fixation were employed. Electron micrographs of ultrathin sections cut normal to the film surface are shown in Figure 2.

The dark portions in the micrographs are the polybutadiene phase stained selectively by osmium tetraoxide. The domains are extremely small. Short rodlike domains

0024-9297/84/2217-1417$01.50/0