Brønsted acids. It is interesting to note that while CCl_3CO_2H has less catalytic activity than $PhSO_3H \cdot H_2O$, the combination of $SnCl_2 \cdot 2H_2O$ and CCl_3COOH provides a greater synergistic catalytic effect than the combination of $SnCl_2 \cdot 2H_2O$ and $PhSO_3H \cdot H_2O$.

The synergism caused by mixed acids may well be ascribed to dual-acid formation, since in certain cases the formation of dual acids of enhanced acidity has been recognized.[7] It must be mentioned that during the course of this investigation Pierce and Frick independently observed synergistic catalytic activity caused by mixing certain metal salts and carboxylic acids in the cross-linking reaction of cellulose with formaldehyde or methylolamide agents.[8]

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Comments on the Proposed Existence of Local Order in Amorphous Polymers below Their Glass-Transition Temperatures as Deduced from Calorimetric Studies

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The appearance of endothermal peaks in the dta, dsc, and heat capacity curves for the glass transitions of several amorphous polymers and the dependence of the endothermal peak heights and positions on the thermal histories of the samples investigated have recently been interpreted[1-4] as evidence for the existence of local intermolecular order in the polymers below the glass-transition temperature, T_g; order which is absent above T_g. When a glassy polymer is heated for a period of time above T_g and then either slowly cooled through the glass transition or quenched to below T_g and annealed, subsequent heating of the sample at a constant rate more rapid than the previous cooling rate[5-7] results[1-7] in an endothermal peak near T_g. For a given cooling rate, the endothermal peak height increases and moves to higher temperatures with an increase in the time of annealing below T_g[1,5] and with an increase in the annealing temperature.[1,4]

Several workers[1-4] have attributed the above-mentioned calorimetric behavior of amorphous polymers in the glass-transition region to the local ordering of the segments of neighboring polymer chains. They[1,3,4] envision the ordering process at temperatures below T_g as a parallel alignment of those portions of neighboring chains having identical configurations and conformations to form a small crystalline area in the otherwise amorphous solid. Upon heating through the glass transition, these crystalline regions are said to be disrupted at the onset of substantial polymer backbone motion, resulting in the observed endothermal peaks at, or slightly above, T_g. It is our view that such an interpretation (crystalline-like order produced by annealing below T_g) of the thermal-history-dependent calorimetric behavior of amorphous polymers in the glass-transition region is invalid, and we qualitatively suggest an alternative explanation based on the dynamic conformational characteristics of polymer chains and the nonequilibrium nature[5-7] of the glassy state of polymers.

The rotational isometric-state model[8] of polymer chains is adopted, where it is assumed that each backbone bond in the chain is constrained to a small number of rotational states (usually three). The frequency of occurrence or the probability of finding a given backbone bond in any of its rotational states depends[8,9] on the rotational states of the adjacent backbone bonds (nearest-neighbor interdependence). Intramolecular and intermolecular excluded-volume effects[9] are assumed to be absent in the undiluted bulk polymer.

Above T_g, each polymer chain is relatively free to adopt any of the myriad of possible rotational isomeric conformations consistent with the restriction that each backbone bond is only able to assume a small number of rotational states. As the temperature is lowered to T_g, the rate of rotational isomerism about each backbone bond is drastically reduced[5] until large-scale backbone motions become severely restricted below the glass transition due to the increased viscous drag at these increased densities (or due to the lack of sufficient free volume[10] to permit these rotational isomerisms). This increase in the viscous drag resisting rotational isomerism stems from the increased cooperativity[5] between the motions of neighboring chains which is made necessary by the increased density (or decreased free volume[10]) below the glass transition. Consequently, as the temperature is dropped rapidly from above T_g through the glass transition, the conformation of each chain becomes further removed[5,6] from its equilibrium conformation at the temperature in question.

The following three predictions are the logical results of the model of bulk amorphous polymers presented above: (i) the customary discontinuity in the heat capacity should be observed at T_g when the cooling and heating rates through the glass transition are equal, (ii) an endothermal peak should appear near T_g when the heating rate exceeds the cooling rate through the glass transition, and (iii) an exothermal peak should appear near T_g when the cooling rate through the glass transition exceeds the heating rate. When the rates of cooling and heating through the glass transition are equal, each chain is removed from its equilibrium conformation to the same extent[5,6] at the same temperature in both legs of the thermal cycle, thus the absence of thermal peaks near T_g. Heating through T_g at a rate exceeding the cooling rate through the glass transition results in each chain adopting a conformation closer to its equilibrium conformation, which corresponds to a lower energy, on the cooling leg of the cycle. Hence, an endothermal peak in the heating leg of the cycle appears near T_g where the chains are more rapidly able to approach their equilibrium conformations. The reverse reasoning predicts the appearance of an

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exothermal peak near T_g when the cooling rate through the glass transition exceeds the heating rate.

All three predictions of the above model are borne out by experimental observations. The heating rates exceeded the cooling rates in each of the calorimetric studies[1-7] where endothermal peaks were observed. However, as noted by Ali and Sheldon[4] (Figure 10), the endothermal peak near T_g disappears as the cooling rate approaches the heating rate. On the other hand, exothermal peaks near the glass transition have been observed[2,11] when the cooling rate exceeded the heating rate.

In addition, the following two calorimetric observations[1,4,5] can also be explained qualitatively by our model of the glassy state of polymers: (i) following quenching from above T_g, the greater the time of annealing below T_g the larger the endothermal peak observed and (ii) at constant anneal time the lower the annealing temperature the smaller the endothermal peak height. Upon quenching from above the glass transition, each chain in the glassy sample is in a conformation corresponding more closely to the equilibrium conformation above T_g than the lower energy equilibrium conformation below T_g. Annealing for long periods of time[5] below T_g permits each chain to approach its equilibrium conformation at T_{anneal}. Hence, when rapidly heated through the glass transition from T_{anneal}, those samples annealed for longer periods of time are further away from their equilibrium conformations at T_g (corresponding to higher energy conformations than those at T_{anneal}) than the samples annealed for short periods of time, and exhibit larger endothermal peaks. The observed shifts of the endothermal peaks to higher temperatures as the annealing period is increased in the annealed samples[5] or as the cooling rate is decreased in the unannealed samples[1] can also be explained on this basis. On the other hand, for a constant anneal time, lowering the temperature of annealing decreases the extent of the approach to the equilibrium conformation at T_{anneal} and results in a decrease in the endothermal peak height.

Briefly summarizing, it is our contention that the observations made in the calorimetric studies of the glass transitions in amorphous polymers are consistent with the concept of unordered polymer chains both above[12] and below T_g. Thus, it is not necessary to invoke[1-4] partial ordering of neighboring chains below the glass transition to explain the appearance of the endothermal peaks observed[1-7] near T_g and their dependence on the thermal history of the sample when the heating rate through the glass transition exceeds the cooling rate. We do not exclude the possibility that short stretches of individual polymer chains adopt an ordered conformation (there is always a finite probability[9] that any consecutive stretch of backbone bonds will simultaneously assume the same conformation), but there is nothing in the calorimetric observations to suggest that the intramolecularly ordered stretches in different chains associate and align to form small areas of crystalline-like intermolecular order. In fact, to invoke the existence of such crystalline order resulting from slow annealing below T_g requires an explanation as to why these minute crystalline regions melt near T_g instead of at the much higher thermodynamic melting temperature.

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Copolymerization of Acrylamide with Sulfur Dioxide

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Although many olefins copolymerize with sulfur dioxide to form polysulfones,[1] the presence of electronegative substituents, such as carbonyl or nitrile, can prevent the copolymerization.[1-5] Thus acrylonitrile homopolymerizes in liquid sulfur dioxide in the presence of a free-radical initiator.[5] It would not be surprising, therefore, if acrylamide and sulfur dioxide did not copolymerize readily.

Some reported experiments would seem to support a low order of reactivity. Cyclopentene, acrylamide, and sulfur dioxide gave a terpolymer without added initiator at 30 and 60°. However, in the absence of cyclopentene, acrylamide and sulfur dioxide did not copolymerize.[6] Sulfur dioxide has been reported to initiate the polymerization of various vinyl compounds but neither acrylamide nor similarly substituted monomers.[7] A patent[8] claims a copolymer of acrylamide and sulfur dioxide made by irradiation at low temperatures (−10 to −200°) with ionizing radiation. While the properties of the copolymer were not given, a subsequent report of a similar system describes a copolymer containing only 1% sulfur.[9] Experiments on the polymerization of acrylamide in liquid sulfur dioxide have also been carried out by Panzer and Cibulskas,[10] of these laboratories, but the product was not fully characterized.

This work was undertaken in order to clarify and extend the previous work on the acrylamide–sulfur dioxide system. Rather unexpectedly, acrylamide was found to copolymerize quite readily with sulfur dioxide under certain conditions.

Experimental Section

The reactions carried out at 50° or lower were done in Pyrex glass pressure reactors. The polymerizations at 80 and 100° were carried out in a 316 stainless steel autoclave. Acrylamide was Cyanamid commercial material, mp 82.5–84.7°. That used in runs 1 and 2 had been sublimed and then stored; mp 83.5–85.5°. Matheson anhydrous sulfur dioxide was used. The nitrate salts were reagent grade except for $Ce(NO_3)_3 \cdot 6H_2O$, CP grade, and ceric ammonium nitrate, obtained from Matheson Coleman and Bell.

An Acrylamide–Sulfur Dioxide Copolymer. A reactor containing 19.98 g (0.2811 mol) of acrylamide and 0.170 g (1.04 mmol) of azobisisobutyronitrile was cooled in liquid nitrogen, evacuated, and brought to atmospheric pressure with dried nitrogen three times. Then the reactor was evacuated and 67.2 g of sulfur dioxide (1.05 mol) was added by transfer in a vacuum line. The mixture was heated at 50° for 8 hr and then allowed to stand overnight at room temperature. The reactor was cooled and the product was washed

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