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.

Acknowledgment. The author is grateful to Drs. H. E. Bair and R. J. Roe for several enlightening discussions.

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(11) H. E. Bair, private communication.

(12) A. E. Tonelli, *J. Chem. Phys.*, **53**, 4339 (1970).

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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(1) Recent reviews: (a) K. J. Ivin and J. B. Rose, *Advan. Macromol. Chem.*, **1**, 335 (1968); (b) N. Tokura in "Encyclopedia of Polymer Science and Technology," Vol. 9, Interscience, New York, N. Y., 1968, pp 460–485.

(2) See ref 1a, pp 352, 358; ref 1b, p 463.

(3) L. L. Ryden and C. S. Marvel, *J. Amer. Chem. Soc.*, **57**, 2311 (1935).

(4) L. L. Ryden, F. J. Glavis, and C. S. Marvel, *ibid.*, **59**, 1014 (1937).

(5) N. Tokura, M. Matsuda, and F. Yazaki, *Makromol. Chem.*, **42**, 108 (1960).

(6) S. Iwatsuki, T. Okada, and Y. Yamashita, *J. Polym. Sci., Part A-1*, **6**, 2451 (1968).

(7) P. Ghosh and K. F. O'Driscoll, *J. Macromol. Sci., Chem.*, **1**, 1393 (1967).

(8) K. Shinohara, Z. Kuri, and T. Yoshimura, Japanese Patent 9971 (1965); *Chem. Abstr.*, **64**, 3799 (1966).

(9) Z. Kuri, *Kobunshi*, **18** (203), 106 (1969).

(10) H. P. Panzer and A. C. Cibulskas, private communication.

TABLE I
POLYMERIZATIONS

Run	Acrylamide, g	SO_2, g	Catalyst, mg	Reaction time (temp, °C)	Polymer, g	η_{inh}[a]
1	1.2	5.5	None	3 days (~25)	Trace	
2[b]	1.2	5.5	MEK peroxide[c]	46 hr (~25)	Small amount	
3	1.0	7.2	Benzoyl peroxide, 13	24 hr (~25)	0.14	
4	15.0	13	$Ce(NO_3)_3 \cdot 6H_2O$, 27	4 days (~25)	14.7	0.22[d]
5	15.0	31.5	$Ce(NO_3)_3 \cdot 6H_2O$, 27	5 days (~25)	16.0	0.76[e]
6	15.0	46	NH_4NO_3, 60	18 hr (~25)	10.9	0.49[e]
7	1.98	8.3	Benzoyl peroxide, 25.5	5.5 hr (50)	0.85	0.51[e]
8	3.75	12.6	AIBN,[f] 32	8 hr (50)	4.3	0.52[e]
9	19.98	67.2	AIBN, 170	8 hr (50)	20.0	0.56[e]
10	10.0	50	AIBN, 85	5 hr (80)	7.3	0.29[g]
11	10.0	50	AIBN, 85	5 hr (100)	8.6	0.33[g]

[a] Determined at 30°, 0.5% concentration. Trace amounts of undissolved polymers were sometimes first removed by filtration. [b] Catalyst was added to the reaction mixture from the first polymerization. [c] Methyl ethyl ketone peroxide. [d] In dimethyl sulfoxide containing 20% water. [e] In dimethyl sulfoxide. [f] Azobisisobutyronitrile. [g] In aqueous 1 *N* sodium nitrate.

TABLE II
ANALYSES OF THE ACRYLAMIDE–SULFUR DIOXIDE COPOLYMERS

Run	Temp, °C	Analyses				Polymer compositions		Acrylamide:SO_2 mol ratio
		% C	% H	% N	% S	Wt % acrylamide[a]	Wt % SO_2	
1	~25	ND[b]	ND	ND	ND			
2	~25	ND	ND	ND	ND			
3	~25	37.37	5.94	14.20	11.42	72.9	22.8	2.88
4	~25	39.18	5.83	14.37	11.25	75.1	22.5	3.01
5	~25	37.96	5.60	13.86	11.56	72.6	23.1	2.83
6	~25	38.12	5.66	14.53	11.41	74.5	22.8	2.94
7	50	39.15	6.19	15.79	8.62	78.7	17.2	4.12
8	50	38.20	6.13	14.89	8.66	75.4	17.3	3.93
9	50	39.34	6.05	14.97	8.94	76.8	17.9	3.87
10	80	44.41	7.05	16.63	4.44	86.0	8.9	8.77[c]
11	100	44.44	6.82	17.06	4.97	87.1	9.9	7.94[c]

[a] The results calculated from carbon and nitrogen analyses were averaged. [b] ND = not determined. [c] These mole ratios are not corrected for the sulfonate detected in the infrared spectra.

out with cold methanol, collected on a filter, washed several times with methanol, and dried *in vacuo* at room temperature and finally at 74–80° *in vacuo* for 18 hr. The yield of white solid was 20.0 g; ir (mineral oil mull) SO_2 bands (cm^{-1}) at 1305 and 1128; C=O at 1665; NH_2 at 3440, 3365, 3205, and 1615. Other properties are given in the various tables under run 9.

Results and Discussion

Additional polymerizations are described in Table I. The polymerizations were conducted in liquid sulfur dioxide solution, from which the polymers precipitated. Methyl ethyl ketone peroxide, benzoyl peroxide, and azobisisobutyronitrile were effective catalysts, as were several nitrates: silver nitrate, calcium nitrate, cerous nitrate, ammonium nitrate, and ceric ammonium nitrate. Ferric nitrate was inactive. A small amount of polymerization, presumably caused by traces of peroxide in the acrylamide,[11] took place in the absence of added initiator. Thus in run 1, the solution of acrylamide in sulfur dioxide soon became cloudy. However, the polymerization stopped after only a trace amount of polymer had formed. Addition of methyl ethyl ketone peroxide then caused the polymerization to resume. The crude products were treated with methanol or acetone and sometimes finally with ethyl ether to remove unchanged acrylamide and by-products.

Strong bands in the infrared spectra of the copolymers at 1128 and 1305 cm^{-1} are characteristic of sulfone groups.[12] Ionic sulfonate absorptions[13] at *ca.* 1040 and *ca.* 1200 cm^{-1} were weak or absent in copolymers made at 25 and 50°, but they were observed in the by-products and in the copolymers made at 80 and 100° in stainless steel autoclaves.

Inherent viscosities of the polymers are given in Table I. All of the copolymers tested became molten between 216 and 226° with gas evolution. In sharp contrast to the solubility of polyacrylamide in water, most of the copolymers were insoluble in water but soluble in dimethyl sulfoxide. The copolymers from runs 4, 10, and 11 were exceptions. The copolymer from run 4 dissolved in aqueous dimethyl sulfoxide, while the copolymers from runs 10 and 11 were mostly soluble in water and also in hot dimethyl sulfoxide.

Compositions of the copolymers, calculated from elemental analyses, are given in Table II. The calculated amounts of acrylamide and sulfur dioxide in the copolymers totaled a few weight per cent less than 100%, and the hydrogen analyses were somewhat higher than expected. A few per cent water in the hydrophilic polymer would account for these observations.

The acrylamide–sulfur dioxide system resembles the vinyl

(11) A. Nakano and Y. Minoura, *Kogyo Kagaku Zasshi*, **71**, 732 (1968).

(12) See ref 1a, p 342.

(13) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 310.

TABLE III

Feed[a]	Copolymer[a]
0.12	2.88
0.29	2.94
0.43	2.83
1.0	3.01

[a] Moles of acrylamide per mole of SO_2.

chloride–sulfur dioxide system[14] in that both give polymers with variable compositions generally containing less sulfur dioxide as the polymerization temperature is increased. The increased amount of sulfur found in the acrylamide–sulfur dioxide copolymer from the 100° run as compared to the polymer from the 80° run is at variance with this trend. The reason for this anomaly is not known. Another similarity to the vinyl chloride system is the absence of much effect, if any, of the feed ratio on the compositions of the polymers formed at room temperature (Table III).

Acknowledgment. We thank members of the Scientific Services Department for the infrared data, elemental analyses, and viscosity data. O. Francesconi helped with the polymerizations done at 80 and 100°, and H. Ando translated some Japanese reports. This project was undertaken at the request of Dr. H. P. Panzer of the Industrial Chemicals and Plastics Division of the American Cyanamid Co.

[14] C. Schneider, J. Denaxas, and D. Hummel, *J. Polym. Sci., Part C*, No. **16**, 2203 (1967).

Influence of Added Oxidants on the π-Crotylnickel Iodide Catalyzed Polymerization of Butadiene

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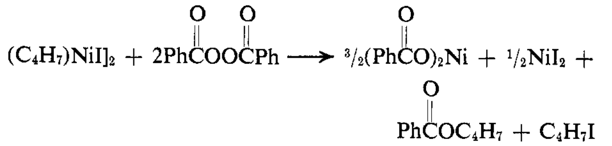
It has been suggested that such additives as oxygen, peroxides, or iodine may influence the activity and stereospecificity of π-crotylnickel halides as butadiene polymerization catalysts.[1-3] We report a series of experiments with crotylnickel iodide which indicate that oxygen, peroxides, and molecular iodine simply destroy the catalyst to produce inactive products. The experiments relate to the effects of the latter additives on the rate of butadiene polymerization, the activation energy of the reaction, and the molecular weights of polymers produced.

Results and Discussion

The effect of added benzoyl peroxide on the rate of butadiene polymerization at constant nickel concentration is shown in Figure 1. In these reactions the catalyst was pretreated with peroxide prior to introduction of monomer. The points shown are experimental rates, while the curve is a theoretical trace calculated on the assumption that catalyst is destroyed according to the reaction

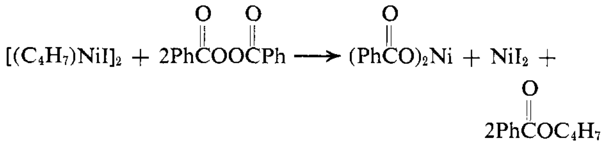


$$\mathrm{(C_4H_7)NiI]_2 + 2Ph\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}Ph \longrightarrow {}^3/_2(Ph\overset{\overset{O}{\|}}{C}O)_2Ni + {}^1/_2NiI_2 + Ph\overset{\overset{O}{\|}}{C}OC_4H_7 + C_4H_7I} \qquad (1)$$

and the rate law for the polymerization is[4]

$$\text{rate} = k_p(k_2/k_{-2})^{1/2}[(C_4H_7NiI)_2]^{1/2}[\text{monpmer}] \qquad (2)$$

Reaction 1 is written as an exact analog of the reaction of phenylmagnesium bromide with benzoyl peroxide.[5] The insoluble nickel salt produced in (1) gave an experimental iodide to benzoate ratio more consistent with the above stoichiometry than that of reaction 3. The close correspondence of the experimental points to the calculated curve of Figure 1 leaves little doubt that the benzoyl peroxide is simply destroying the crotylnickel iodide dimer on a two-to-one molar basis. Similar results were obtained for molecular oxygen and iodine. The latter reagent destroyed crotylnickel iodide dimer on a 1:2 molar basis, but difficulties in measuring small quantities of oxygen made accurate determination of the stoichiometry of its reaction with crotylnickel iodide difficult. The effect of O_2 on polymerization rate is illustrated in Figure 2. It may be reasonably assumed that the apparent stoichiometry of 0.3 mol of O_2 per mole of nickel actually corresponds to reaction 4, where



$$\mathrm{[(C_4H_7)NiI]_2 + 2Ph\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}Ph \longrightarrow (Ph\overset{\overset{O}{\|}}{C}O)_2Ni + NiI_2 + 2Ph\overset{\overset{O}{\|}}{C}OC_4H_7} \qquad (3)$$

$$2[(C_4H_7)NiI]_2 + O_2 \longrightarrow \text{products} \qquad (4)$$

the products are totally inactive.

In a second series of experiments a sample of catalyst was partially destroyed by reaction with benzoyl peroxide and the resulting catalyst was used to determine the activation energy of the polymerization reaction. The temperature coefficient was identical with that obtained with unadulterated catalyst, and when account was taken of destruction of the catalyst according to (1), the Arrhenius plots for pure catalyst and catalyst–benzoyl peroxide reactions were superimposable within experimental error, as shown in Figure 3.

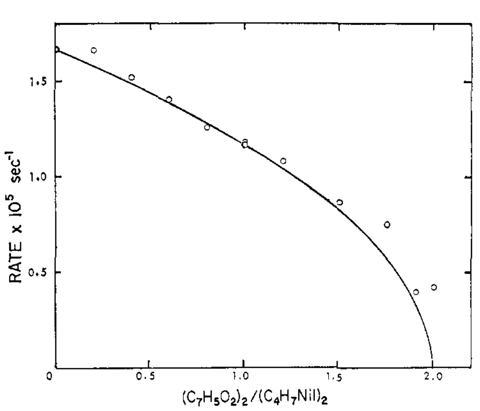


Figure 1. Effect of added benzoyl peroxide on the apparent rate coefficient (rate/$[C_4H_6]$); $[(C_4H_7NiI)_2]$ = 0.005 *M*, $[C_4H_6]$ = 1.5 *M*, temperature = 50°: ○, experimental points; ———, computed curve.

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[1] J. Furukawa and H. Morimura, *J. Polym. Sci., Part B*, **7**, 541 (1969).

[2] J. Matsumoto, J. Furukawa, and H. Morimura, *ibid., Part B*, **6**, 869 (1969).

[3] J. Matsumoto, J. Furukawa, and H. Morimura, *ibid., Part A-1*, **9**, 875 (1971).

[4] J. F. Harrod and L. R. Wallace, *Macromolecules*, **2**, 449 (1969).

[5] S. Lawesson and N. C. Yang, *J. Amer. Chem. Soc.*, **81**, 4230 (1959).