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FACTORS INFLUENCING POLYSULFONE FORMATION. II. A NEW METHOD OF INDUCTION WITH CONTROL OF POLYMER LENGTH

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Received July 2, 1948

In a previous paper (1) it has been shown that a mixture of ascaridole and hydrogen bromide is effective in inducing the heteropolymerization of sulfur dioxide and olefins, which ordinarily gives poor yields of polysulfones. Many other polymerizing agents of varying efficacy are known (2). The most efficient of these are those generally recognized as producing free radicals in solution, namely, light, oxygen, and peroxidic materials. With none of the agents previously studied can the length of the polymer chain be controlled, the products being polymers of the molecular weight range of 50,000 to 200,000.

It has been shown in this laboratory (3) that bromotrichloromethane is dissociated by light into bromine atoms and free trichloromethyl radicals which can initiate free-radical chain reactions. We have found that bromotrichloromethane when irradiated by light can initiate the copolymerization of sulfur dioxide and olefins. The length of the polymer chain depends on the ratio between the concentrations of bromotrichloromethane and sulfur dioxide. By variation of this ratio the nature and length of the polymer chain can be controlled.

The reactions involved may be formulated as follows:

$$\mathrm{BrCCl_3} + h\nu \rightarrow \mathrm{Br}\cdot + \mathrm{Cl_3C}\cdot \tag{1}$$

$$\mathrm{RCH=CH_2} + \mathrm{Cl_3C}\cdot \rightarrow \cdot\mathrm{CHRCH_2CCl_3}\ (\mathrm{I}) \tag{2}$$

$$(\mathrm{I}) + \mathrm{BrCCl_3} \rightarrow \mathrm{BrCHRCH_2CCl_3}\ (\mathrm{II}) + \mathrm{Cl_3C}\cdot \tag{3a}$$

$$(\mathrm{I}) + \mathrm{SO_2} \rightarrow \cdot\mathrm{SO_2CHRCH_2CCl_3} \tag{3b}$$

$$\cdot\mathrm{SO_2CHRCH_2CCl_3} + \mathrm{RCH=CH_2} \rightarrow \cdot\mathrm{CHRCH_2SO_2CHRCH_2CCl_3}\ (\mathrm{III}) \tag{4}$$

$$(\mathrm{III}) + \mathrm{BrCCl_3} \rightarrow \mathrm{BrCHRCH_2SO_2CHRCH_2CCl_3}\ (\mathrm{IV}) + \mathrm{Cl_3C}\cdot \tag{5a}$$

$$(\mathrm{III}) + \mathrm{SO_2} \rightarrow \cdot\mathrm{SO_2CHRCH_2SO_2CHRCH_2CCl_3} \tag{5b}$$

$$\begin{aligned}&\cdot\mathrm{SO_2CHRCH_2SO_2CHRCH_2CCl_3} + \mathrm{RCH=CH_2} \rightarrow\\ &\qquad \cdot\mathrm{CHRCH_2SO_2CHRCH_2SO_2CHRCH_2CCl_3}\ (\mathrm{V})\end{aligned} \tag{6}$$

Bromotrichloromethane and sulfur dioxide compete with each other in reactions 3*a* and 3*b*, 5*a* and 5*b* for the free radicals I and III. Radical V can react, as did radical III in reactions 5*b* and 6, with sulfur dioxide and the olefin to yield higher polymerized material, or it can react with bromotrichloromethane, as in reaction 5*a*, to yield a polysulfone. Therefore, the polysulfone molecules produced from this bromotrichloromethane-induced polymerization of sulfur dioxide and an olefin contain n molecules of sulfur dioxide, $n + 1$ molecules of olefin, and one molecule of bromotrichloromethane. Furthermore, the average molecular weight of the polymer is determined by the ratio of sulfur dioxide to bromotrichloromethane in the competing reactions *3a vs. 3b*, *5a vs. 5b*, etc.

Table I illustrates the control of polymer size for the reaction of 1-octene with sulfur dioxide by varying the ratio of sulfur dioxide to bromotrichloromethane. Since the polymers contain both sulfur and halogen it is possible to calculate the average value of n from the silver equivalent and the per cent of sulfur in the compound utilizing the equation $n = \text{Ag Equiv.} \times \%S/801.5$.[1]

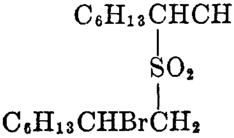
From experiments made with equimolar quantities of bromotrichloromethane and sulfur dioxide with 1-octene, a viscous oil is obtained by molecular distillation. The oil is 1,1,1-trichloro-3-nonyl 2-bromooctyl sulfone (VI), whose structure is in accord with the reaction scheme outlined.[2] This product definitely has not the head-to-head, tail-to-tail structure (VII) analogous to that suggested by the studies of Marvel and co-workers (4) on propylene and pentene polysulfones.

TABLE I

CONTROL OF POLYMER SIZE IN 1-OCTENE POLYSULFONE FORMATION

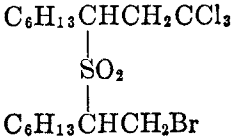
RUN	RATIO $BrCCl_3/SO_2$	NATURE OF THE POLYMER	%S	Ag EQUIV.	MOL. WT.*	n
2	2/5	Viscous oil	6.96	122.2	500	1.0
3	1/6	Sticky, taffy-like glass	14.36	295.7	1200	5.3
4	1/10	Pliable solid	16.10	478	1900	9.6
6	1/65	Brittle solid	18.94	2874	11,000	68

* Four times Ag Equiv.



$$\begin{array}{c} C_6H_{13}CHCH_2CCl_3 \\ | \\ SO_2 \\ | \\ C_6H_{13}CHBrCH_2 \end{array}$$

(VI)



$$\begin{array}{c} C_6H_{13}CHCH_2CCl_3 \\ | \\ SO_2 \\ | \\ C_6H_{13}CHCH_2Br \end{array}$$

(VII)

EXPERIMENTAL

Polysulfone formation induced by bromotrichloromethane. Method one. A quarter of a mole of olefin and the desired amount (from 0.01 to 0.1 mole) of bromotrichloromethane were placed in a Pyrex tube and degassed on a vacuum line. The desired amount of sulfur dioxide (0.3 to 0.8 mole) was condensed into the tube which was then sealed. The sealed tube was shaken between two 100-watt Mazda lamps placed one foot from the tube. After several days of radiation the tube was opened, and the excess sulfur dioxide and olefin were distilled. Any small quantity of olefin-bromotrichloromethane addition product (such as 1,1,1-trichloro-3-bromononane obtained from 1-octene) was removed by heating the

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[1] The term Ag equiv. is defined as the number of grams of the halogen-containing compound which react with one mole of silver nitrate, in accordance with the reaction:

$$Ag^+ + X^- \rightarrow AgX$$

[2] Details of proof of structure are presented in the Experimental Part.

reaction mixture to 50° at 10^{-5} mm. In the cases of nearly equal molar ratios of bromotrichloromethane to sulfur dioxide, the tube contents were subjected to molecular distillation. The results obtained by this method are recorded in Table II.

Method two. Bromotrichloromethane (1.1 mole, 220 g.) and 1-octene (1.3 mole, 150 g.) were placed in a tube internally illuminated by a mercury vapor-neon fluorescent coil and sulfur dioxide was bubbled into the solution through a sintered-glass gas disperser. By this method 180 g. of 1,1,1-trichloro-3-bromononane, 50 g. of 1,1,1-trichloro-3-nonyl 2-bromooctyl sulfone (VII), and 50 g. of higher-molecular-weight polysulfones were obtained in eleven hours.

Identification of heavy oil obtained by molecular distillation from the reaction of 1-octene and sulfur dioxide in the presence of bromotrichloromethane (1,1,1-trichloro-3-nonyl 2-bromooctyl sulfone). Subjection of the reaction product of 1-octene with nearly equal quantities of sulfur dioxide and bromotrichloromethane to molecular distillation yielded a heavy oil, n_D^{20} 1.5028. The heavy oil does not react with cold alcoholic silver nitrate and thus does not contain any SO_2Br groups.

TABLE II

RESULTS OF REACTIONS BY METHOD ONE

RUN	OLEFIN (MOLE)	$BrCCl_3$ (MOLE)	SO_2 (MOLE)	RATIO $BrCCl_3/SO_2$	WT. ADDUCT (G.)	WT. POLYMERS (G.)	%S	Ag EQUIV.	n[c]
2	C_8H_{16}, 0.25	0.12	0.31	2/5	18[a]	$\left.\begin{matrix}2\\16\end{matrix}\right\}^{d}$	6.96 15.23	122.2 342.2	1.0 6.5
3	C_8H_{16}, 0.25	0.12	0.78	1/6	2[a]	50	14.36	295.7	5.3
4	C_8H_{16}, 0.25	0.06	0.60	1/10	4[a]	60	16.10	478	9.6
6	C_8H_{16}, 0.25	0.012	0.78	1/65	1.5[a]	40	18.94	2874	68
7	C_3H_5Cl, 0.25	0.12	0.60	1/5	3[b]	7	11.19	79.6	2

[a] 1,1,1-Trichloro-3-bromononane.

[b] 1,1,1,4-Tetrachloro-3-bromobutane.

[c] For octene n = %S × Ag Equiv./801.5; for allyl chloride n = 5 × %S × Ag Equiv./(3206 − %S × Ag Equiv.).

[d] The 2-gram fraction was removed from the 16-gram fraction by molecular distillation. This 2-g. fraction corresponds to an adduct of one mole of bromotrichloromethane to one mole of sulfur dioxide to two moles of 1-octene.

Anal. Calc'd for $C_{17}H_{32}BrCl_3O_2S$: S, 6.60; Ag Equiv., 121.7; Mol. Wt., 486.6.

Found: S, 6.96, 7.23, 7.07; Ag Equiv., 122.5, 122.2, 125.5; Mol. Wt., (by f.p lowering of benzene) 500.5, 500.0.

The heavy oil can be titrated in alcoholic solution with cold alcoholic KOH. One molecule of hydrogen bromide is lost and an olefin is obtained.

Anal. Calc'd for $C_{17}H_{31}Cl_3O_2S$: S, 7.92; Ag Equiv., 135.2.

Found: S, 7.89; Ag Equiv., 134.3.

The olefin was subjected to ozonization in ethyl acetate solution at −60°. The ethyl acetate was evaporated at reduced pressure, and the resulting ozonide decomposed with water. The mixture was extracted with ether. The ether extract was washed with aqueous sodium carbonate and steam-distilled. The residue from the steam distillation contained sulfur and chlorine. The steam distillate yielded a red-orange 2,4-dinitrophenylhydrazone, which melted at 125–126°. This hydrazone proved to be identical with that obtained on refluxing an authentic sample of hexaldehyde with hydrochloric acid and treating the product with 2,4-dinitrophenylhydrazine. The authentic 2,4-dinitrophenylhydrazone of the dehydrated aldol of hexaldehyde melted at 126–127°, and its melting point was not depressed by admixture with the hydrazone of the aldol obtained from ozonization.

Anal. Calc'd for $C_{18}H_{26}N_4O_4$: C, 59.8; H, 7.2; N, 15.5.
Found: C, 61.3; H, 6.8; N, 15.6.

A careful search for formaldehyde in the water-soluble fractions and in the ethyl acetate from the ozonization proved fruitless.

SUMMARY

A new method for the induction of the heteropolymerization of sulfur dioxide and olefins by means of bromotrichloromethane and light is described, and the mechanism of reaction is discussed.

The control of polymer molecular weight by varying the relative concentrations of bromotrichloromethane and sulfur dioxide is demonstrated.

The simplest one-link polymer of sulfur dioxide and 1-octene formed in the presence of bromotrichloromethane is shown to be 1,1,1-trichloro-3-nonyl 2-bromooctyl sulfone.

CHICAGO 37, ILL.

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