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Vinyl Polymerization Initiated by Sulfur Dioxide

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Summary

A number of monomers have been polymerized in the presence of catalytic and higher concentrations of SO_2. The addition of *t*-butyl hydroperoxide greatly accelerates the rate of polymerization. The use of $^{35}SO_2$ indicates that at catalytic concentrations of SO_2 (10^{-2} mole/liter), only one or two molecules of SO_2 are incorporated in the chain, but, at high SO_2 concentrations, copolymerization of SO_2 with vinyl monomers occurs.

It has been reported in a preliminary communication (*1*) that sulfur dioxide at low concentrations can initiate polymerization of methyl methacrylate and styrene but fails to initiate polymerization of some other vinyl monomers such as acrylonitrile, vinyl acetate, methyl acrylate, acrylamide, acrylic acid, and α-methyl styrene. The present paper reports the results of further investigations on the use of sulfur dioxide as initiator of vinyl polymerization.

EXPERIMENTAL

Baker anhydrous sulfur dioxide of 99.98% purity, supplied in cylinders, was used without further purification. When polymerization of methyl methacrylate (MMA) was carried out in the presence of a solvent, the initiator solution was prepared by bubbling SO_2 through a well-cooled volume of the respective sol-

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vent. The concentration of SO_2 in solution was determined by standard iodometry. For bulk polymerization of MMA, the initiator solution was prepared by bubbling SO_2 gas from the cylinder through a well-cooled volume of MMA, and the SO_2 content was determined iodometrically. It was found by running a control titration in the presence of MMA that the iodometric titration of SO_2 was not notably affected by the presence of MMA. For the polymerization of all other monomers, SO_2 dissolved in methanol (dried over CaH_2 and distilled) was used as the initiator solution. All acrylate and methacrylate monomers, acrylonitrile, styrene, vinyl acetate, isoprene, vinyl pyridine, and allyl acetate, were dried over CaH_2 and distilled under a reduced pressure of nitrogen before use. Acrylamide from the Borden Chemical Co. was used as received and acrylic acid was purified by drying over anhydrous sodium sulfate and then by vacuum distillation. t-Butyl hydroperoxide supplied by the Borden Chemical Co. was used without further purification. ACS analytical-grade and spectro-grade pyridine were also used without any treatment. The procedure for polymerization under vacuum was similar to that described previously (*1*).

RESULTS AND DISCUSSION

Methacrylates (methyl, ethyl, and butyl) have been easily polymerized by sulfur dioxide in the concentration range 10^{-1}–10^{-4} mole/liter and in the temperature range 0–60°C. Polymerization of styrene has also been possible, but the rate of polymerization is relatively slow. Isoprene has been very easily polymerized in 50% (v/v) solution in methanol only when the concentration of sulfur dioxide is fairly high, i.e., of the order 0.5–2 mole/liter.

SO_2 has been found to be ineffective to induce polymerization of the acrylates (methyl and ethyl), acrylonitrile, acrylamide, acrylic acid, vinyl acetate, allyl acetate, 4-vinyl pyridine, and α-methyl styrene. Thus it appears that vinylidene monomers ($CH_2{=}CXY$) are easily polymerizable while those with one substitution ($CH_2{=}CHX$) fail to give polymers, the two exceptions being styrene and α-methyl styrene.

Polymerization of Methyl Methacrylate by SO_2

Polymerization of MMA was done in bulk, in methanol solution, and in pyridine solution over a wide range of initiator SO_2 concentrations: 5×10^{-4} to 3 mole/liter. The initial rate of polymerization in bulk increases with increasing SO_2 concentration and passes through a maximum at about 0.007–0.008 mole/liter SO_2 concentration. It then sharply falls to a low intermediate value and remains more or less unchanged on further increase in SO_2 concentration. Figure 1 shows such plots at three different temperatures, initial

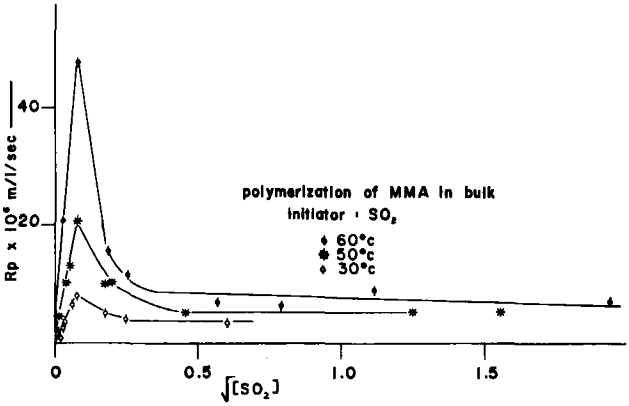

FIG. 1. Initial rate of bulk polymerization of MMA vs. square root of SO_2 concentration at 60°, 50°, and 30°C.

rates being plotted against square root of initiator concentration. Below about 0.008 mole/liter SO_2 concentration, a linear plot with a positive slope is obtained. Intercepts at zero SO_2 concentration for polymerizations at 60 and 50°C give the expected uncatalyzed thermal rates of polymerization. The polymerization is autocatalytic in nature beyond about 10% conversion, possibly because of the high viscosity of the initial polymer, whose intrinsic viscosity in benzene at 30°C was of the order of 5–6 $(g/dl)^{-1}$. The polymer molecular weight also increased with increasing conversion. Polymerization in methanol media also conforms more or less to the same pattern. Activation energy for bulk polymerization is found to be about 6.4 kcal/mole with SO_2 concentration less than 0.008 mole/liter, the Arrhenius plot being shown in Fig. 2. The kinetic studies were made on the basis of gravimetric analysis of polymer formed, the polymer being isolated by precipitation with petroleum ether. In polymerization in methanol the initial rate R_p is found to be proportional to the 1.5 power of monomer concentration. Hence

$$R_p = K[SO_2]^{0.5}[M]^{1.5} \qquad (1)$$

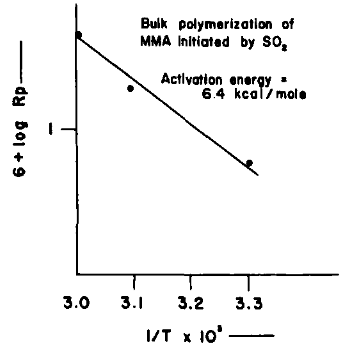

FIG. 2. Arrhenius plot of bulk polymerization of MMA initiated by SO_2.

when $[SO_2]$ is less than 0.008 mole/liter. Thus the polymerization process may be a radical process, with the initiation step involving a monomer molecule.

Polymerization of MMA by SO_2 in pyridine solution has been found to be largely irreproducible. The polymerization rate is much higher with ACS analar-grade pyridine than with spectrograde pyridine. A white precipitate was found to separate out when SO_2 solution in ordinary or ACS analar-grade pyridine was mixed with MMA, which could be easily dissolved on slight warming. With spectro-grade pyridine, however, little or no precipitation

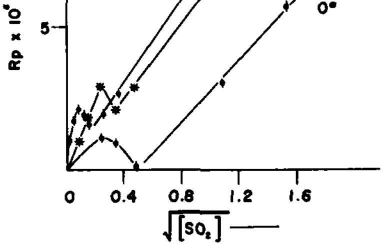

FIG. 3. Initial rate of polymerization of MMA in spectro-grade pyridine at 50° (O), 20° (°), and 0°C (●).

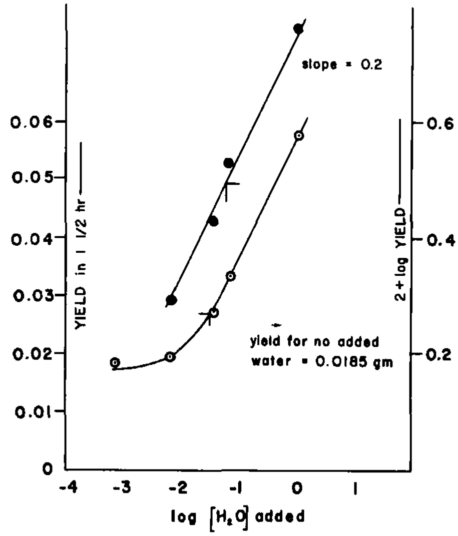

FIG. 4. Influence of water on polymerization of MMA initiated by SO_2 in spectro-grade pyridine.

occurred. Polymerization in spectro-grade pyridine shows a maximum and a minimum, respectively, in initial rate with increasing SO_2 concentration, and finally the rate increases with the initiator concentration (Fig. 3). The presence of variable amounts of adventitious impurities in different samples of pyridine and the formation of a 1:1 complex between SO_2 and pyridine (2) are factors influencing the polymerization. Water at low concentrations ($< 10^{-2}$ mole/liter), when added to spectro-grade pyridine, did not change the rate measurably, but a higher concentration of water was found to enhance the rate; a plot of log (rate) against log $[H_2O]$, Fig. 4, gives a straight line in the higher concentration range of water with a slope of about 0.2.

Polymerization Initiated by a SO_2–*t*-Butyl Hydroperoxide System

Easy and rapid polymerization of the common monomers such as the methacrylates (methyl, ethyl, and butyl), acrylates (methyl and ethyl), acrylonitrile, vinyl acetate, and styrene was obtained with a SO_2–*t*-butyl hydroperoxide initiator system. Of these, the polymerization of the acrylates was found to be the fastest, the reaction being induced almost instantaneously with high heat buildup;

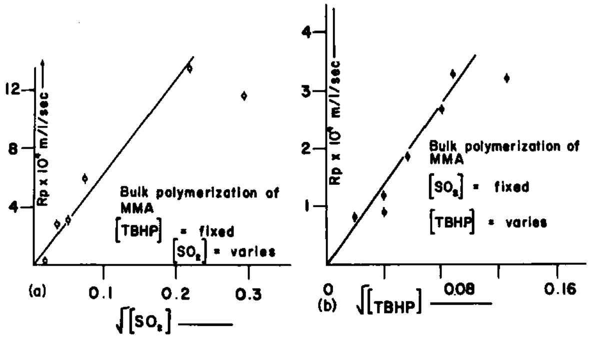

FIG. 5. Rate of bulk polymerization of MMA initiated by the system TBHP–SO_2: (a) [TBHP] = 8×10^{-3}; (b) [SO_2] = 2×10^{-3}.

within a few minutes after initiation, polymerization was complete to 50–80%. Next to the acrylates was acrylonitrile, which also polymerized rapidly but with somewhat less heat buildup. Polymerization was not inhibited in the presence of small amounts of hydroquinone or other commercial stabilizers with the SO_2–*t*-butyl hydroperoxide pair as the initiator.

The yield curves of MMA polymerization at fixed SO_2 concentration and varying *t*-butyl hydroperoxide (TBHP) concentration (and vice versa) were measured. The *initial* rate of polymerization of MMA passes through a maximum with increasing hydroperoxide or SO_2 concentration; and below the concentration of the initiator components at which the maximum occurs, the rate is proportional to the square root of SO_2 and hydroperoxide concentration at fixed hydroperoxide and SO_2 concentration respectively (Fig. 5) and to

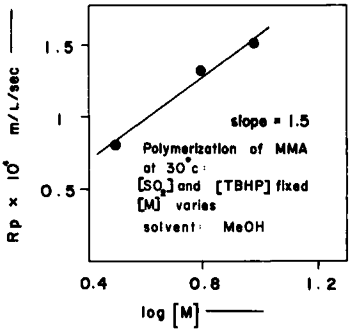

FIG. 6. Influence on rate of polymerization of MMA initiated by SO_2–TBHP of varying MMA concentration by addition of methanol.

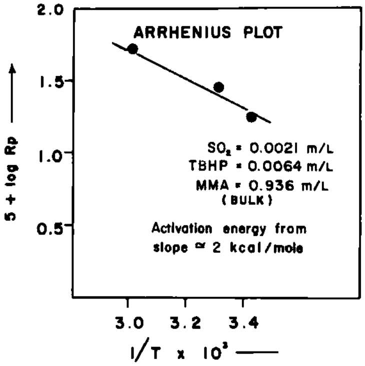

FIG. 7. Arrhenius plot of bulk polymerization of MMA initiated by SO_2–TBHP.

the 1.5 power of the monomer concentration, the concentration of the monomer being varied by the addition of methanol in the system (Fig. 6). Thus the rate may be expressed as

$$R_p = K([SO_2][TBHP])^{0.5}[M]^{1.5} \tag{2}$$

The activation energy of overall polymerization in the temperature range 30–60°C is about 2 kcal/mole, the Arrhenius plot being shown in Fig. 7. The intrinsic viscosity of the polymer has been found to increase with conversion, and this is presented in Fig. 8 for a single set of polymerizations.

Incorporation of Sulfur Dioxide in Polymer

No sulfur was detectable in the SO_2-initiated poly(methyl methacrylate) by the application of conventional methods. Applica-

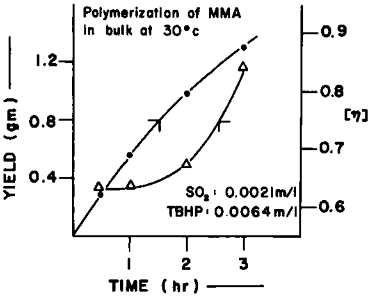

FIG. 8. Yield and intrinsic viscosity of polymer from bulk polymerization of 2 ml of MMA with $[SO_2] = 2.1 \times 10^{-3}$ and $[TBHP] = 6.4 \times 10^{-3}$ at 30°C.

tion of the sensitive-dye-partition technique with aqueous methylene blue reagent and chloroform solution of the polymers (3) indicated the presence of some sulfoxy groups in the polymers, but a quantitative application of this method was impossible because the method was developed for the analysis of anionic sulfoxy groups such as sulfate (SO_4^-) and sulfonate (SO_3^-), and the nature of the sulfoxy groups incorporated in the present polymers either at the ends or in any part of the chain was uncertain and presumably not ionic. The very high molecular weight of the polymers also made them unsuitable for quantitative analysis by this technique.

Polymers of isoprene obtained by sulfur dioxide initiation in methanolic media were found to be cross-linked and thus insoluble in any solvent of polyisoprenes. They were, however, found to contain nearly 0.7–1.0 mole of sulfur dioxide per 2 isoprene units, the analysis being done by the usual method of oxidation by nitric

TABLE 1

Determination of SO_2 Incorporated in Poly(methyl methacrylate)

						Mole SO_2 in polymer	
SO_2, mole/liter	MMA, ml	Pyridine, ml	Other reagents	Temp. °C	$\bar{M}_n \times 10^{-5a}$	per chain	per base mole
0.29	4.0	—	—	25	48.7	38	0.00077
0.19	6.0	—	—	25	50.1	18.4	0.00036
0.19	6.0	—	—	50	38.1	3.8	0.0001
0.019	4.0	—	—	25	58.4	—	—
0.42	6.0	—	0.3% TBHP	25	1.92	14	0.0073
0.019	6.0	—	0.3% TBHP	25	3.89	7.7	0.002
0.42	6.0	—	0.05% Bz_2O_2	25	39.2	14.1	0.00036
0.19	6.0	—	0.05% Bz_2O_2	50	12.7	1.1	0.00008
0.29	3.9	0.1	—	25	31.2	1.9	0.000063
0.29	3.9	0.1	—	50	24.1	3.4	0.00014
0.29	3.5	0.5	—	25	19.9	2.2	0.00011
0.29	3.0	1.0	—	25	18.1	6.4	0.0036
0.29	2.0	2.0	—	25	5.88	22.1	0.0037
0.29	2.0	2.0	—	0	11.9	42	0.0035
0.29	2.0	2.0	1% water	25	3.57	28	0.0076
0.072	2.0	2.0	—	25	7.73	5.3	0.00069
0.0072	2.0	2.0	—	25	8.92	3.6	0.0004

[a] $\bar{M}_n$ was calculated from $[\eta]^{30°}_{C_6H_6}$ values with the use of the equation (8) $\bar{M}_n = 2.81 \times 10^5 [\eta]^{1.32}$.

TABLE 2

Copolymerization of MMA and Styrene Initiated by Sulfur Dioxide

Styrene, ml	MMA, ml	SO_2[a] in feed, g	Other reagents	Temp., °C	Conversion, %	SO_2 in copolymer, %	Styrene in copolymer, %
1.07	1.0	0.047	—	25	6	14	42
1.07	1.0	0.047	—	50	8	2.3	43
1.07	1.0	0.047	—	0	5	22	—
1.07	1.0	0.047	0.3% TBHP	25	6	15	42
1.07	1.0	0.047	0.3% TBHP	50	5	2.1	—
1.07	1.0	0.047	1 ml pyridine	25	6	4.1	40
2.14	0.2	0.0094	—	25	3	1.7	68
2.14	0.2	0.0094	0.3% TBHP	25	8	3.8	63
1.07	1.0	0.047	0.05% Bz_2O_2	25	3	12.1	43
1.07	1.0	—	0.1% Bz_2O_2	60	6	—	50
2.14	0.2	—	0.1% Bz_2O	60	8	—	84

[a] SO_2 dissolved in MMA was used as initiator, the gas being liberated by heating sulfuric acid (containing 4% ^{35}S-labeled sulfuric acid) with copper turnings.

acid and bromine and then precipitating the sulfuric acid formed as barium sulfate. The high SO_2 content of the isoprene polymers might be due to the addition of SO_2 at the double bonds of the polyisoprene formed with consequent formation of intramolecular cyclic polysulfone with occasional formation of intermolecular linkage giving the cross-linked product.

Some polymerization experiments were done in the presence of ^{35}S-labeled SO_2. ^{35}S-labeled sulfuric acid diluted with inactive sulfuric acid in a 1:25 ratio was heated in the presence of copper turnings and the sulfur dioxide liberated was bubbled through cold MMA; this solution of SO_2 in MMA was used in a few polymerization and copolymerization experiments. The polymers were isolated at low conversions and purified by double precipitations and then dried in vacuum at 50°C. The sulfur content of the purified polymers or copolymers was determined by comparing the radioactive counts given by a known amount (0.004–0.008 g) of the polymers in thin-film form (prepared in aluminum planchets of 2 cm diameter from chloroform solution of the respective polymers) with that given by a known amount (0.005 g) of $BaSO_4$ prepared from the acid mixture from which the initiating SO_2 was generated. The $BaSO_4$ planchet was prepared by spreading a thin suspension of the finely powdered salt in chloroform on the planchet and then drying it under vacuum at 50°C. The results, given in Tables 1 and 2, must be regarded as somewhat approximate because of the possibility of self-absorption by the samples of the weak β particles from ^{35}S. A solution of thermally polymerized poly(methyl methacrylate) in chloroform was mixed with active SO_2 in methanol. The polymer was then purified by double precipitation and dried under vacuum and showed complete absence of radioactivity; thus the possibility of the presence of radioactivity in the test samples due to physically bound SO_2 is ruled out.

It is seen from Table 1 that polymers of MMA bear some SO_2 groups in them and that the SO_2 content varies with the condition of the experiments. The number of moles of SO_2 incorporated in the polymers appears to be dependent on the concentration of SO_2 used; lower SO_2 concentration incorporates lesser amounts of SO_2. Only very trace or negligible activity was observed in the polymers prepared in bulk if the concentration of the initiator was less than 0.02 mole/liter, but for polymers prepared in the presence of pyridine and SO_2, measurable activity was obtained when the initiator SO_2 concentration was as low as 0.005 mole/liter. Starting with bulk polymerization at 25°C and gradually increasing pyridine concentration at constant volume and constant SO_2 concentration, it was found that a small amount of pyridine lowered the amount of SO_2 incorporated, but at high pyridine concentration the molecular weight of the polymers was appreciably lowered and the SO_2 content in them notably enhanced. An increase in the temperature of polymerization usually decreased SO_2 incorporation; this is more apparent in the copolymerization of MMA and styrene (Table 2). In the presence of *t*-butyl hydroperoxide, SO_2-initiated polymerization was greatly accelerated, the molecular weight was lowered, and the incorporation of SO_2 in the polymer increased appreciably.

In the copolymerization of MMA and styrene, it has been found (*1*) that the copolymers obtained generally show a lower styrene content [as determined by UV spectroscopy (7)] than expected for a normal free-radical polymerization. At least for high SO_2 concentrations, this is understood to be due to the introduction of some sulfur dioxide in the copolymers, and instead of being a case of binary copolymerization it is a case of terpolymerization of MMA, styrene, and SO_2. Some of the copolymers obtained were found to be partially insoluble in chloroform. It is also apparent from the two tables that the incorporation of SO_2 is much more pronounced when MMA is copolymerized with styrene than when MMA is polymerized alone by SO_2.

Mechanism

The exact mechanism of SO_2-initiated vinyl polymerization seems to be somewhat complex. The easy polymerizability of the methacrylates (and to a much less effective extent of styrene) and the failure to polymerize the acrylates, acrylonitrile, vinyl acetate, acrylamide, acrylic acid, allyl acetate, etc., indicate the importance of the steric influence of substituents on the double bond of the monomers. A very similar observation was made when bisulfite ion was used to initiate aqueous vinyl polymerization (*4*), where the phenomenon was explained by considering the formation of bisulfite addition compounds with singly substituted monomers, styrene being the exception.

In the present case, the failure to polymerize, by SO_2, singly substituted monomers of the type $CH_2{=}CHX$ may be explained by a probable formation of cyclic sulfones due to addition of SO_2 to the monomeric unsaturation; with the methacrylates and styrene this is hindered, probably because of the steric influence of the substituents, and the result is probably a biradical formation:

$$SO_2 + CH_2{=}CXY \rightleftharpoons \dot{S}O_2{-}CH_2{-}\dot{C}XY \qquad (3)$$

Recently, Zutty et al. (5) reported a spontaneous copolymerization of 2,2,1-hept-2-ene and sulfur dioxide to yield living polysulfone (1 : 1) by a biradical initiation and propagation by biradical coupling, the polymerization being carried out in liquid sulfur dioxide at low temperatures. In the present case, square-root dependence of rate on initiator SO_2 concentration suggests a bimolecular termination of polymerization of MMA. All the experimental evidence suggests that a polysulfone structure of trace SO_2 content is obtained. During the propagation step, participation of a sulfur dioxide–monomer complex or a biradical formed as shown above seems to take place, probably with reversibility of this propagation step.

It has been found that the polymerization of MMA at 30°C was completely inhibited in the presence of acetic acid: a cationic mechanism of polymerization can thus be precluded. The retardation of polymerization at relatively high SO_2 concentration thus appears to be due to the relatively high acidic nature of the medium. Inhibition of polymerization by hydroquinone is also indicative of the radical nature of the polymerization process.

The polymerization process initiated by a *t*-butyl hydroperoxide–sulfur dioxide system appears still more complex. All the common vinyl monomers are polymerizable by this system and hydroquinone does not seem to inhibit polymerization. This may indicate the process to be other than radical in nature. But the kinetics of the MMA polymerization suggest it to be a radical process with bimolecular termination and an initiation step involving one molecule each of SO_2, *t*-butyl hydroperoxide, and the monomer. Schulz and Banihaschein (*6*) polymerized styrene in liquid sulfur dioxide in the presence of certain peroxides or hydroperoxides and reported a high rate of polymerization of styrene, which they suggest to have taken place by a cationic mechanism, but in the presence of solvents. Polystyrene sulfones were obtained by a radical process with a much decreased rate.

In the present system, where SO_2 was used at very low concentrations, polymerization was found to be uninhibited in the presence of alcoholic solvents and traces of moisture. When the hydroperoxide–sulfur dioxide system was used to polymerize α-methyl styrene at room temperature for about 48 hr under vacuum and then poured in methanol, no polymer was found to separate out; but on keeping the whole system with nonsolvent in air for a few days, some polymer of a sticky nature was found to separate out. These points need further investigation.

Acknowledgment

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Zusammenfassung

Eine Anzahl Monomerer wurde in Gegenwart katalytischer und höherer Konzentrationen von SO_2 polymerisiert. Zugabe von *t*-Butylhydroperoxid beschleunigt die Polymerisation beträchtlich. Durch Verwendung von $^{35}SO_2$ ergab sich, dass bei katalytischen SO_2 Konzentrationen (10^{-2} m/l) nur ein bis zwei SO_2 Moleküle in die Ketten eingebaut werden. Bei hohen SO_2 Konzentrationen hingegen tritt Kopolymerisation von SO_2 mit Vinylmonomeren ein.

Résumé

On a polymerisé quelques monomères en présence de SO_2 en concentrations catalytiques et en concentrations plus elevées. L'addition du t-butylhydroperoxide augmente beaucoup la vitesse de polymérisation. L'emploi de $^{35}SO_2$ indique qu'une ou deux molecules de SO_2 sont seulement incorpores dans la chain en présence de concentrations catalytiques de SO_2. Les concentrations de SO_2 plus elevées provoquent une copolymérisation de SO_2 avec des monomères vinyliques.

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