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Copolymerization of Styrene and Liquid Sulfur Dioxide in the Presence of α-Toluenethiol, 1-Butanethiol, or Bromotrichloromethane

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We have carried out copolymerization (telomerization) of styrene and liquid sulfur dioxide (liq. SO_2) in the presence of α-toluenethiol, 1-butanethiol, or bromotrichloromethane by using a radical initiator (AIBN) in order to study of the propagation mechanism in styrene polysulfone formation.

It is well known that aliphatic olefins, such as ethylene and propylene, always form alternate copolymers with SO_2 by a radical initiator. Kharasch and Friedlander obtained telomers (**1** and **2**), by copolymerizing octene-1 and SO_2 in the presence of bromotrichloromethane, but no telomer having $-SO_2Br$ group.[1] Styrene also copolymerizes with SO_2, but unlike aliphatic olefin forms copolymers having various compositions.[2]

$CCl_3CH_2CH(C_6H_{13})Br$
(**1**)

$CCl_3CH_2CH(C_6H_{13})S(O_2)CH_2CH(C_6H_{13})Br$
(**2**)

We have obtained the following telomers (**3**, **4**, and **5**) (the head to tail structure of the first styrene unit in product **5** could not be confirmed) in the case of α-toluenethiol.

$C_6H_5CH_2SCH_2CH_2(C_6H_5)$
(**3**)

$C_6H_5CH_2SStStH$
(**4**)

$C_6H_5CH_2SStS(O_2)StH$
(**5**)

$(St{=}{-}CH_2CH(C_6H_5){-})$

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[1] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **13**, 882 (1948).

[2] M. Matsuda and M. Iino, *Macromolecules*, **2**, 216 (1969).

The propagation steps in this chain reaction are considered to be as follows.

$$\mathrm{C_6H_5CH_2S\cdot + CH_2{=}CH(C_6H_5) \longrightarrow \underset{(A)}{C_6H_5CH_2SSt\cdot}} \qquad \text{(a)}$$

$$\mathrm{A + CH_2{=}CH(C_6H_5) \longrightarrow \underset{(B)}{C_6H_5CH_2SStSt\cdot}} \qquad \text{(b)}$$

$$\mathrm{A + SO_2 \longrightarrow \underset{(C)}{C_6H_5CH_2SStSO_2\cdot}} \qquad \text{(c)}$$

$$\mathrm{C + CH_2{=}CH(C_6H_5) \longrightarrow \underset{(D)}{C_6H_5CH_2SStS(O_2)St\cdot}} \qquad \text{(d)}$$

$$\mathrm{A, B, D + C_6H_5CH_2SH \longrightarrow}$$

$$\text{Product, } \mathbf{3, 4, 5} + \mathrm{C_6H_5CH_2S\cdot} \qquad \text{(e)}$$

As in the case of octene-1 – SO_2 system,[1] the telomer with $-SO_2H$ group expected to be formed by termination of (C) radical was not obtained. We carried out copolymerization in the presence of 1-butanethiol or bromotrichloromethane. In these cases also the telomer having $-SO_2H$ group or $-SO_2Br$ (in the case of bromotrichloromethane) group was not obtained. This is probably due to the fact that either the sulfonyl radical is inert to hydrogen abstraction reaction from thiol (and bromine abstraction reaction from bromotrichloromethane) or the life time of sulfonyl radical is very short compared to that of styryl radical at this temperature (60°C).

Structures of products **3**, **4**, and **5** suggest that styrene polysulfone has head to tail structure.

The photo-decomposition of α-toluenethiol or 1-butanethiol in liq.SO_2 was also carried out and only disulfide which was formed by coupling reaction of thiyl radicals was obtained. Sulfone expected to be formed from the reaction of thiyl radical with SO_2 was not obtained.

Experimental

Materials. Styrene, azobisisobutyronitrile (AIBN) and liq. SO_2 were purified by the method described previously.[3] α-Toluenethiol and 1-butanethiol were purified by distillation. Bromotrichloromethane was prepared[4] from bromine and chloroform and distilled just before use.

Telomerization with α-Toluenethiol. 9.0 g (0.09 mol) of styrene, 10.8 g (0.09 mol) of α-toluenethiol, 29.7 g (0.46 mol) of liq. SO_2 and 0.5 g (0.003 mol) of AIBN, were charged in a reaction vessel,[3] and reacted at 60°C for 8 hr. Unreacted liq. SO_2, styrene and α-toluenethiol were then distilled off and the residue was chlomatographed on an alumina column. The liquid obtained by elution with petroleum ether was distilled under a reduced pressure. The distillate (161—164°C/1.5 mmHg) gave 11.8 g (58% yield based on styrene) of **3**, $C_6H_5CH_2SStH$ (St$=-CH_2CH(C_6H_5)-$). Found: C, 79.30; H, 7.04; S, 13.96%. Calcd for $C_{15}H_{16}S$: C, 78.90; H, 7.06; S, 14.04%. NMR (CCl_4): τ, 2.9—3.1 (10H, phenyl), 6.5 (2H, $-CH_2S-$), 7.1—7.7 (4H, $-CH_2CH_2(C_6H_5)$). The residue of the distillation gave about 1 g (6%) of **4**, $C_6H_5CH_2SStStH$, identified as sulfoxide and sulfone by oxidation using $KMnO_4$ in $CHCl_3$. Sulfoxide ($C_6H_5CH_2S(O)$-$StStH$). Found: C, 78.55; H, 6.89; S, 9.51%. Calcd for $C_{23}H_{24}SO$: C, 79.27; H, 6.94; S, 9.20%. Mp 122—125°C (recrystallized from methanol), IR 1020 cm^{-1} (SO). Sulfone ($C_6H_5CH_2S(O_2)StStH$); mp 102—103°C (recrystallized from methanol), lit,[5] 98—99.5°C, IR 1300, 1120 cm^{-1} (SO_2). Elution with ether gave 0.8 g (4%) of (5), $C_6H_5CH_2SStS(O_2)StH$. Found: C, 69.55; H, 6.03; S, 15.98%; mol wt (mass spectrum) 396. Calcd for $C_{23}H_{24}S_2O_2$: C, 69.66; H, 6.10; S, 16.17%; mol wt 396.6. mp 116.5—118°C, NMR ($CDCl_3$): τ, 2.4—3.1 (m, 15H, phenyl), 5.9—6.1 (quar, 1H, $-CH-$), 6.5 (s, 2H, $C_6H_5C\underline{H}_2-$), 6.4—7.0 (2H, $-S(O_2)CH_2-$), 7.0—7.3 (m, 4H, $-SCH_2-$, $-C\underline{H}_2(C_6H_5)$), showed no methyl group expected from head to head structure of terminal styrene unit.

Telomerization with 1-Butanethiol. 9.0 g (0.09 mol) of styrene 8.3 g (0.1 mol) of 1-butanethiol, 28.7 g (0.45 mol) of liq. SO_2 and 0.5 g (0.003 mol) of AIBN were reacted at 60°C for 30 hr. By the same procedure as in the case of α-toluenethiol, C_4H_9SStH, (7.8 g, 45%), $C_4H_9SStStH$ (about 0.5 g, 4%) and $C_4H_9SStS(O_2)StH$(0.3 g, 2%) were obtained. C_4H_9SStH. Found: C, 74.41; H, 9.56%. Calcd for $C_{12}H_{18}S$: C, 74.19; H, 9.34%. Bp 88—89°C/<1 mmHg, lit,[6] 96—97°C/1 mmHg. $C_4H_9SStStH$. Speculated from its boiling point (>100°C/<1 mmHg, lit[6] 170°C/1 mmHg), IR spectrum (almost the same as that of C_4H_9SStH) and refractive index (n_D^{25}, 1.5524, lit,[6] 1.5539). $C_4H_9SStS(O_2)StH$. Found: C, 66.05; H, 7.24%. Calcd for $C_{20}H_{26}S_2O_2$: C, 66.26; H, 7.23%. IR 1310, 1130 cm^{-1} (SO_2).

In the reactions using 18 g (0.18 mol) and 36 g (0.36 mol) of styrene, we obtained 0.2 g and 2 g, respectively, of styrene polysulfone other than the products described above.

Telomerization with Bromotrichloromethane. 36.0 g (0.36 mol) of styrene, 40 g (0.2 mol) of CCl_3Br, 168 g (2.6 mol) of liq. SO_2 and 4 g (0.02 mol) of AIBN were reacted at 60°C for 42 hr. By the same procedure as described above, about 20 g (18%) of CCl_3StBr was obtained. We carried out the reaction with various feed compositions, but could not obtain the telomer having $-SO_2Br$ group. CCl_3StBr. Found: C, 35.94; H, 2.50%. Calcd for $C_9H_8BrCl_3$: C, 35.74; H, 2.67%. Mp 51.5°C, lit,[7] 54—55°C.

Photo-decomposition of α-Toluenethiol in Liq. SO_2. A mixture of 10.8 g (0.09 mol) of α-toluenethiol and 28.6 g (0.45 mol) of liq. SO_2, was charged in a quartz vessel, and irradiated with a 300 W mercury lamp (high-pressure) at room temperature for 24 hr. Unreacted SO_2 and α-toluenethiol were distilled off. The residue gave 4.5 g (41% yield based on α-toluenethiol) of $(C_6H_5CH_2S)_2$, identified from IR spectrum of an authentic sample. Only $(C_4H_9S)_2$ was obtained in the case of 1-butanethiol.

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3) N. Tokura and M. Matsuda, Kogyo Kagaku Zasshi, **64**, 501 (1961).

4) L. I. Zakharkin, *Chem. Abstr.*, **48**, 547a (1954).

5) H. Miyoshi and R. Oda, *Kogyo Kagaku Zasshi*, **59**, 224 (1956).

6) K. Yamagishi, *Nippon Kagaku Zasshi*, **80**, 1361 (1959).

7) M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Amer. Chem. Soc.*, **69**, 1105 (1947).