mation. No polymer was produced by applying 5kV/cm to an α-methylstyrene–DCE solution ($[\alpha\text{-MSt}]_0$ = 0.80 mol/l.) without BF_3OEt_2 for 5 hr. This result implies that the polymerization can be started neither by an direct electron transfer to monomer nor by an electrolysis of solvent. Furthermore, we subjected a catalyst solution ($[BF_3OEt_2]_0 = 1.1 \times 10^{-4}$ mol/l.) to an electric field (1.6 kV/cm) for 2 hr before the monomer was added and carried out the polymerization in the absence of the field. The observed polymerization rate agreed with that obtained by using a catalyst solution without the preelectrolysis treatment. According to this finding, it is highly improbable that active species were produced electrolytically from the catalyst and solvent.

The molecular weight of the polymer produced was not reproducible and the field influence on this quantity was undetectable.

Communications to the Editor

The Solvent Effect on the Composition of Styrene Polysulfone

It is well known that the aliphatic olefins, such as ethylene, propylene, and the butenes, form alternating copolymers with liquid sulfur dioxide by means of a radical initiator.[1] Styrene also copolymerizes with liquid sulfur dioxide radically, and forms styrene polysulfones having various copolymer compositions. The composition depends mainly on the polymerization temperature but hardly on the feed composition.[2,3] These results suggest that the familiar equation for copolymer composition, *i.e.*, the Mayo/Lewis equation, cannot be applied to the copolymerization of the styrene/liquid sulfur dioxide system. Thus, Barb[1] has introduced the concept of participation of a 1:1 styrene/liquid sulfur dioxide complex in propagation in order to interpret the kinetics of the copolymerization of styrene with liquid sulfur dioxide. However, an entirely equivalent scheme can be derived without invoking complex participation.[4] Concerning this matter, we have already been investigating the copolymerization of various styrene derivatives with liquid sulfur dioxide, but we could not clarify the mechanism of the propagation.[5-7] The present paper is concerned with the solvent effect on the composition of styrene polysulfone, and the results obtained here offer a key for the solution of the propagation mechanism.

The radical copolymerization of styrene and liquid sulfur dioxide was carried out with α,α′-azobisisobutylonitrile (AIBN) as an initiator at 50 and 80°. The mole fraction of styrene in the feed was kept constant at 0.8 or 0.2, but the initial total monomer concentration of styrene and liquid sulfur dioxide was varied from 1.0 to 9.0 mol/l. by adding such solvents as *o*-dichlorobenzene, cyclohexane, sulfolane, nitrobenzene, and pyridine, respectively. With the exception of the cyclohexane solvent, polymerization proceeds in a homogeneous system. After allowing the copolymerization to proceed to not more than 5% conversion, the copolymer was isolated into methanol, and then it was reprecipitated from dioxane/methanol. The composition of copolymer was determined by carbon analysis.

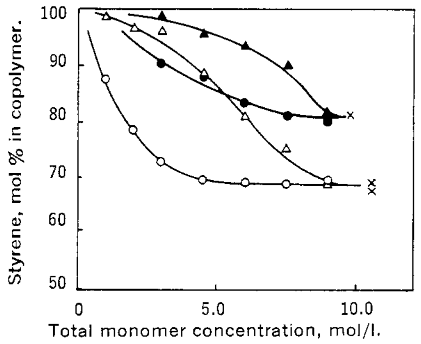

Figure 1. Copolymer composition curves which were obtained from pyridine [—△— (50°), —▲— (80°)] and sulfolane [—○— (50°), —●— (80°)] as added solvents, respectively. The styrene mole fraction in feed was kept constant at 0.8.

The results of the copolymerizations at 50° are summarized in Tables I and II, in which the styrene feed compositions were kept constant at 0.8 and 0.2, respectively. From these tables, it can be seen that the copolymer compositions at fixed feed composition vary not only with the nature of solvents used, but also with the initial total monomer concentrations. The typical results are plotted in Figure 1. It is most likely from Tables I and II and Figure 1 that the solvent effect can be divided into two groups, that is, pyridine and the remaining solvents of which sulfolane is a representative example. The styrene mole fraction in the copolymer increases by the addition of pyridine, which is known to form a strong charge-transfer complex with liquid sulfur dioxide.[8] With the other solvents, mutual interaction with liquid sulfur dioxide is rather small, and it does not have an effect in a region of comparably higher monomer concentrations. However, even in these solvents, at lower monomer concentrations, the styrene mole fraction in the copolymer increases with increasing solvent volume fraction.

It is quite possible to interpret this dilution effect as a characteristic of polymerization involving a charge-transfer complex, providing that a depropagation has

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TABLE I

EFFECT OF THE SOLVENTS ON THE COMPOSITION OF STYRENE POLYSULFONE (50°)[a]

Styrene, mol % in feed	Total monomer concn, mol/l.	Added solvent, vol %	Styrene, mol % in copolymer: o-Dichlorobenzene	Cyclohexane	Sulfolane	Nitrobenzene	Pyridine	Bulk
80	1.0	89.8	89.4		87.3		98.6	
80	2.0	79.6	80.4		78.9		96.5	
80	3.0	69.4	77.7	77.9	72.7	74.6	96.0	
80	4.5	54.1	73.8	71.7	69.5	72.7	88.6	
80	6.0	38.9	72.4	71.7	69.2	70.9	81.0	
80	7.5	23.6	69.9	69.3	68.8	67.6	75.2	
80	9.0	8.3	67.9	68.4	69.5	68.3	68.9	
80	10.7	0.0						68.4[b]

[a] $[AIBN]_0 = 7.5 \times 10^{-3}$ mol/l. [b] The mean value from two experiments (67.8 and 69.0).

TABLE II

EFFECT OF THE SOLVENTS ON THE COMPOSITION OF STYRENE POLYSULFONE (50°)[a]

Styrene, mol % in feed	Total monomer concn, mol/l.	Added solvent, vol %	Styrene, mol % in copolymer: o-Dichlorobenzene	Sulfolane	Pyridine	Bulk
20	3.0	81.3	74.8		91.4	
20	4.5	71.9	71.6	69.2	82.3	
20	6.0	62.5	69.9	69.0	73.5	
20	7.5	53.1	67.9	66.6		
20	9.0	43.8	67.1	66.3	66.2	
20	12.8	0.0				66.6

[a] $[AIBN]_0 = 7.5 \times 10^{-3}$ mol/l.

not occurred. In this case, the copolymer compositions depend on the concentration of the styrene and liquid sulfur dioxide complex, and it should vary with total monomer concentration; *i.e.*, the higher the solvent content the lower the complex concentration. The composition should also depend on the polymerization temperature and the addition of a solvent which has a mutual interaction with liquid sulfur dioxide.

However, an alternative explanation for the dilution effect may be possible if considerable depropagation occurs in these copolymerization systems. It is well known that the radical copolymerizations of liquid sulfur dioxide with a number of aliphatic olefins are characterized by depropagation. As depropagation and propagation are first- and second-order reactions, respectively, the decrease in the rate of depropagation due to dilution is smaller than that in propagation; the result is variable copolymer compositions. In this case, the increase in styrene content by dilution may be interpreted as the result of the increase in the depropagation rate relative to that in propagation.

$$\sim St - SO_2\cdot \longrightarrow \sim St\cdot + SO_2$$

Therefore the possibility of a copolymerization which proceeds by separate monomers (styrene and liquid sulfur dioxide) cannot be discounted completely on the basis of our results, since they can be explained kinetically on the basis of the copolymerization of separate monomers involving a depropagation. The results of the detailed investigation will be presented in the near future.

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Electron Spin Resonance Evidence of Inactive V(III) Precursor to Catalytically Active V(III) in Vanadium Tetrachloride Ziegler Catalysts

In a recent paper[1] on the active oxidation state of vanadium in soluble monoolefin polymerization catalysts, one of us presented data in support of the thesis that catalytically active V(III) species came from inactive V(III) complexes. Earlier, other workers[2] had suggested that the inactive precursor was a V(IV) complex. We now present esr data which support our conclusion that the catalyst precursor was an inactive V(III) complex. Furthermore, the esr results are consistent with the view[1] that the active species was an alkylvanadium(III) complex and that the precursor contained no alkylvanadium bonds.

In the synthesis of syndiotactic polypropylene with a Et_2AlCl–VCl_4 catalyst at −78°, steady-state conditions may be reached after 5–10 hr with a minimum of

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