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Polymerization of Vinyl Monomers in Organic Solutions of Cellulose

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ABSTRACT

Methyl methacrylate and other monomers were polymerized in systems involving cellulose completely or partially dissolved in complex solvents. Both the system [dimethylsulfoxide-sulfur dioxide] and the system [dimethylformamide-copper nitrate-cumene hydroperoxide] were found to be effective in initiating polymerization. In the presence of air, cellulose seemed to counteract the inhibiting effect of oxygen. All the reactions resulted in the formation of homopolymer only, and no graft copolymers of cellulose were detected in the products.

INTRODUCTION

A number of papers have been recently published on the solubility of cellulose in various complex bi- or multicomponent solvents. Typically, such solvents consist of an organic solvent such as dimethylsulfoxide (DMSO) and an additive such as paraformaldehyde or sulfur dioxide.

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Relatively little has been reported on cellulose grafting in such systems. Guthrie et al. [1] grafted styrene onto cellulose by a photochemical method in the DMSO-paraformaldehyde solvent. Tsuzuki and co-workers [2, 3] used γ -radiation to initiate the grafting of styrene onto cellulose in a ternary solvent consisting of DMSO, SO_2 , and diethylamine.

It is well known that sulfur dioxide can initiate polymerization through the formation of charge-transfer complexes [4-6]. When graft copolymerization is conducted in such a solvent, SO_2 can be thought of not only as a cosolvent, but also as a component of the initiation system.

Monomers, for their part, can also participate in the initiation process by forming charge-transfer complexes. For example, Hussain and co-workers [7] investigated the polymerization of methyl methacrylate (MMA) in DMSO and dimethylformamide (DMF) by a charge-transfer complex. They used aliphatic amines to form a charge-transfer complex with MMA and carbon tetrachloride as chain transfer agent. Using the same monomer, Matsuda et al. [8] found that the system sulfur dioxide pyridine-carbon tetrachloride and DMF was the most effective among those tested.

It has been reported by Gaylord [9] that cellulose is also able to form charge-transfer complexes which initiate polymerization. It appeared interesting to investigate whether conditions conducive to polymerization (and, in particular, graft copolymerization) might exist in solutions of cellulose in complex solvents with various additives. Methyl methacrylate was used as the monomer in most experiments.

EXPERIMENTAL

Copolymerization under Inert Atmosphere

The reaction was conducted in a 100 mL, three-neck flask provided with a condenser, a thermometer, and a gas inlet tube equipped with a sintered glass disperser. A tube packed with P_2O_5 granules was attached to the top of the condenser to keep out moisture. In a typical experiment the reactor was charged with 0.8 g of dry cellulose, SO_2 dissolved in DMSO to give a desired final concentration of SO_2 , and, finally, the volume of the mixture was adjusted to 80 mL by adding DMSO. The temperature of the mixture was then brought up to 85°C using an oil bath, and the system was flushed with nitrogen for 20 min. The cellulose became swollen and partly dissolved during this period. Next, 8.0 g MMA (0.935 mol/L) was added and the reaction was allowed to proceed for 2 h. A magnetic stirrer was employed to agitate the reaction mixture. The reaction was terminated by pouring the reaction mixture into excess methanol, and the products were isolated by filtration.

Copolymerization in the Presence of Oxygen

The reaction was conducted in 50 mL Erlenmeyer flasks equipped with rubber stoppers. In a typical experiment the flask was charged with 0.5 g dry cellulose, SO₂ in a solution of DMSO to give a desired final concentration of SO₂, and, finally, DMSO to obtain a final volume of 45 mL. The mixture was then brought up to the desired temperature while being stirred with a magnetic stirrer. The monomer was then added (4.0 g of MMA or 0.831 mol/L) and the reaction was allowed to proceed for 4 h. Polymerization was then terminated by pouring the reaction mixture into methanol, and the products were isolated by filtration.

Preparation of SO₂ Solution in DMSO or DMF

A two-neck round-bottom flask was used. The flask was first filled with the solvent to 2/3 of its volume and then SO₂ was introduced from a cylinder through a glass tube equipped with a sintered glass gas disperser. A magnetic stirrer was used to improve the dissolution of sulfur dioxide. The concentration of SO₂ was determined by iodometric titration and was in the range 6.7-15.5 mol/L.

Preparation of Nitrogen Dioxide Solution in DMF

Nitrogen dioxide, generated by the reaction between copper shavings and HNO₃, was first dried by passing it through a tube filled with P₂O₅. Subsequently it was introduced through a gas disperser into DMF in a two-neck round-bottom flask. The blue color of the solution turned deeper as more N₂O₄ became absorbed in the solvent. The concentration of N₂O₄ in the solution was determined by titration.

Extraction

The reaction products obtained by precipitation in methanol were subjected to Soxhlet extraction to determine the amount of homopolymers. The solvents used were acetone for poly(methyl methacrylate) and DMF for polyacrylonitrile. The DMF extractions were conducted under vacuum to minimize degradation.

Reagents

The monomers were purified by distillation under vacuum. All other reagents were used as supplied by the manufacturers.

RESULTS AND DISCUSSION

The results of the polymerization of MMA in DMSO under nitrogen are shown in Table 1. The presence of SO_2 is necessary to initiate polymerization, as thermal polymerization at this temperature gives nearly zero polymer yield. There does not seem to be any clear dependence on SO_2 concentration in the range studied. A conversion maximum at 0.222 mol/L SO_2 , observed in the presence of α -cellulose, all but disappears when cellulose is absent. The SO_2 -cellulose ratio corresponding to this maximum is about 4 mol SO_2 per mol of glucose unit. It is interesting to note that Tsuzuki et al. [2] also reported maximum conversion of styrene at a molar ratio of cellulose (in moles of glucose units) to SO_2 -diethylamine complex of 1:4. However, unlike the work of the above authors who used mutual γ -irradiation to initiate polymerization, no graft copolymer was formed in the present work, and the polymer was completely removed from the products by acetone extraction. Initiation by SO_2 takes place in the aqueous phase and, evidently, no transfer or termination on cellulose occurs which might lead to the formation of graft copolymer.

It is well known that oxygen is an inhibitor of radical polymerization. The experiments conducted in the presence of air are shown in Table 2. It is seen that oxygen completely inhibits the polymerization of MMA carried out in the absence of cellulose. On the other hand, polymerization of MMA carried out in the presence of cellulose

TABLE 1. Effect of SO_2 and α -Cellulose on the Polymerization of MMA in DMSO^a

α -Cellulose	SO_2 , mol/L	Conversion, %
Present	0.056	17.0
"	0.222	36.2
"	0.888	22.4
Absent	0.056	26.5
"	0.222	31.2
"	0.888	28.6
"	0.000	1.5

^aReaction conditions: Temperature = 85°C, nitrogen atmosphere.

TABLE 2. Effect of Oxygen and α -Cellulose on the Polymerization of MMA in DMSO and DMF^a

α -Cellulose	Atmosphere	Conversion, %	
		DMSO	DMF
Absent	Nitrogen	31.3	13.6
Absent	Air	Traces	-
Present	Nitrogen	36.2	14.0
Present	Air	26.0	21.4

^aReaction conditions: Temperature = 85°C, [SO₂] = 0.222 mol/L.

is only partly inhibited by oxygen. This protective role of cellulose is evident both in the DMSO-SO₂, the DMF-SO₂, and the DMF-SO₂ systems.

The next series of experiments was conducted with CCl₄ as an additive. Carbon tetrachloride is a well-known chain transfer agent, and the difference in reactivity between the original radicals and those formed by chain transfer can lead to an increase or a decrease in the rate of polymerization. The data in Table 3 show that under an inert atmosphere, CCl₄ increases the conversion due to thermal polymerization (from 1.5 to 7.9%). Added cellulose increases the

TABLE 3. Effect of CCl₄ on the Polymerization of MMA in DMSO^a

CCl ₄ , mol/L	SO ₂ , mol/L	α -Cellulose, g/L	Conversion, %
-	-	-	1.5
0.13	-	-	7.9
0.13	-	10	15.5
-	0.222	-	31.3
0.13	0.222	-	28.2
-	0.222	10	36.2
0.13	0.222	10	17.9

^aReaction conditions: Temperature = 85°C, nitrogen atmosphere.

TABLE 4. Effect of Cellulose Type on the Polymerization of MMA in DMSO-SO₂ Mixture^a

Cellulose	Conversion, %	
	0.12 mol/L CCl ₄	No CCl ₄
Cellulose powder	49.9	21.8
Bleached kraft (softwood)	47.3	35.8
Bleached kraft (hardwood)	34.6	25.1
Thermomechanical pulp	57.2	32.5

^aReaction conditions: Temperature = 80°C, air atmosphere.

conversion even further (15.5%). However, addition of CCl₄ has a negative effect on the polymerization of MMA initiated by SO₂, especially in the presence of cellulose, where a 50% decrease in conversion was recorded.

This effect is not repeated in reactions conducted in the presence of air (Table 4). In fact, a converse effect is observed, regardless of the kind of cellulose/pulp used. Even in the absence of CCl₄, it is evident that the presence of any cellulosic product counteracts the inhibiting effect of oxygen. This is in agreement with the result obtained with α -cellulose (Table 2). It appears that thermomechanical pulp is the most effective for enhancing polymerization.

In the experiments presented so far, cellulose was always either completely or almost completely dissolved in the solvent. Such reactions produced no graft copolymer, and conversion to homopolymer was also quite low. An attempt was made to use another system in which most of the cellulose was only swelled by the organic solvent and only a small part of the cellulose was actually dissolved. Polymerization was then started by adding initiators. These polymerizations were conducted in the presence of air.

It is known that metal salts such as Cu(NO₃) form complexes with cellulose and can initiate polymerization in the presence of chain transfer agents [10]. Hydroperoxides are also widely used as initiators of radical polymerization. Table 5 shows that under the experimental conditions used, copper nitrate does not initiate the polymerization of MMA regardless of the cellulose. On the other hand, cellulose seems to increase considerably the conversion of MMA initiated by either cumene hydroperoxide (CHP) alone or by the mixed initiator CHP-Cu(NO₃)₂. Acrylamide and acrylonitrile are polymerized to high conversions by the same initiation system.

Table 6 shows the effect of some additives on the polymerization of MMA in DMSO. Blank experiments have shown that neither CCl₄

TABLE 5. Polymerization of Different Monomers in DMSO with Several Initiating Systems^a

Monomer	Cellulose powder	Initiator	Temperature, °C	Conversion, %
Methyl methacrylate	Absent	Cu ^b	50	0
"	"	Cu	80	0
"	"	CHP ^c	80	16.3
"	"	Cu + CHP	50	2.5
"	"	Cu + CHP	80	4.2
"	Present	Cu	50	0
"	"	Cu	80	0
"	"	CHP	50	16.9
"	"	CHP	80	98.5
"	"	Cu + CHP	50	23.6
"	"	Cu + CHP	80	24.5
Acrylamide	"	Cu + CHP	50	71.1
"	"	Cu + CHP	80	92.0
Acrylonitrile	"	Cu + CHP	80	95.4

^a[Cellulose] = 11.1 g/L, air atmosphere.

^bCopper nitrate, $\text{Cu}(\text{NO}_3)_2$ (1.48×10^{-3} mol/L).

^cCumene hydroperoxide (0.088 mol/L).

not SO_2 is capable of initiating the polymerization of MMA. Both compounds also inhibit polymerization of the same monomer initiated by CHP. Sulfur dioxide alone did not initiate polymerization, but it did so in the presence of CCl_4 and cellulose. The former additive was much less effective (22.4% conversion) than the latter (81.5% conversion). Interestingly, addition of CCl_4 and cellulose in the absence of CHP resulted in the formation of polymer. In general, addition of SO_2 to CHP with or without the presence of other additives reduced the amount of polymer formed.

The last system investigated involved the mixture DMF- N_2O_4 as a solvent for cellulose. Nitrogen dioxide is also known as an initiator of radical polymerization. The results obtained with MMA as the monomer were discouraging in that only very low conversions to polymer were obtained, and the work was consequently abandoned.

TABLE 6. Effect of Reaction Conditions on the Polymerization of MMA in DMSO^a

CHP, mol/L	SO ₂ , mol/L	Cellulose powder, g/L	CCl ₄ , mol/L	Conversion, %
0.088	-	-	-	16.3
-	0.241	-	-	0
-	-	11.1	-	0
-	-	-	0.115	0
0.088	-	11.1	-	24.5
0.088	0.241	-	-	0
0.088	-	-	0.115	0
-	0.241	11.1	-	22.4
-	0.241	-	0.115	81.5
-	-	11.1	0.115	14.1
0.088	-	11.1	0.115	44.0
0.088	0.241	-	0.115	0
0.088	0.241	11.1	-	1.3
-	0.241	11.1	0.115	44.9
0.088	0.241	11.1	0.115	23.5

^aReaction conditions: Temperature = 80°C, air atmosphere.

None of the experiments described above gave rise to the formation of cellulose graft copolymers. It is thus evident that to obtain such copolymers, it is necessary to produce radicals on the cellulosic backbone itself rather than to rely on chain termination and/or transfer by cellulose molecules. It is nonetheless surprising that not even traces of graft copolymers have been detected in the reaction product.

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