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The Cationic Grafting of Styrene onto Poly(4-chloromethylstyrene-co-butadiene)

Z. Janović and K. Sarić

Research Institute, INA, Zagreb, Croatia, Yugoslavia

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The graft copolymerization of styrene onto poly(4-chloromethylstyrene-co-butadiene) with diethylaluminium chloride or stannic chloride as cationic coinitiators was studied in 1,2-dichloroethane or cyclohexane solutions. The backbone polymer was prepared by polymerization of butadiene and 4-chloromethylstyrene in emulsion using $K_2S_2O_8$ as an initiator. Copolymers containing different amounts of chlorine were obtained by changing the ratio of monomers in the monomer mixture.

The grafting percentage and grafting efficiency generally increased by increasing chlorine content in the backbone polymer. Under described conditions, Et_2AlCl gave higher grafting efficiency in comparison with the results obtained when $SnCl_4$ was used as a coinitiator.

INTRODUCTION

Great interest has been shown in recent years for the graft-copolymerization by the cationic methods as an alternative to the well known free radical methods. It was shown by several authors that initiation in cationic polymerization could be effected not only with small molecules but also with suitable macromolecules functioning as initiators in conjunction with a proper coinitiators. By this system a series of graft copolymers have been synthesized. Plesch¹ used conventional Friedel-Crafts catalysts for styrene polymerization in the presence of polyvinyl chloride and Minoura *et al.*² polymerized styrene using $SnCl_4$ in the presence of chlorinated and brominated butyl rubber. Kockelberg and Smets³ used chloromethylated polystyrene as a backbone for grafting isobutene and Overberger⁴ grafted styrene on poly(methoxy styrene). The above systems of graft copolymerization resulted in products with large amounts of homopolymer besides graft copolymers, because these initiators also easy initiate the polymerization of monomer alone. In contrast, Kennedy⁵ has described a series of cationic initiators for graft copolymerization based on certain alkylaluminium compounds in conjunction with halogen containing high polymers. The terminology used for initiating system in this work was according to the same author⁶. In addition, using polymer molecules containing a terminal tertiary halogen atom it was possible to prepare the block copolymers also^{7,8}. Using the same principle Y. Jolivet and J. Peyrot⁹ obtained graft copolymer by reacting styrene onto chloromethylated poly(styrene-b-isobutylene) which was in turn synthesized by polymerization of isobutylene in the presence of partially chloromethylated styrene oligomers. The final graft produced by this

initiators contained negligible amounts of homopolymer because homopolymerization can occur only by chain transfer.

The present work deals with the preparation of the backbone polymer, poly(4-chloromethylstyrene-co-butadiene) by emulsion polymerization of butadiene and 4-chloromethyl styrene and the grafting reaction of styrene onto reactive chloromethyl sites. The reaction was performed using $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ or SnCl_4 as coinitiators in solution, and mixtures of graftcopolymer and polystyrene were obtained. The purpose of the present work was the examination of the influence of the initiator system on the grafting reaction. The formation of graft copolymer was confirmed by extraction of the reaction product with methyl ethyl ketone, a solvent specific for polystyrene, and by infrared spectra of the residue. Percentage of grafting and grafting efficiency were calculated from the increase in weight of the backbone polymer.

RESULTS AND DISCUSSION

Preparation of Poly(4-chloromethylstyrene-co-butadiene)

Poly(4-chloromethylstyrene-co-butadiene) was prepared by copolymerization of 4-chloromethylstyrene and butadiene following the usual procedure for polymerization of styrene and butadiene in emulsion¹⁰. The synthesis of 4-chloromethylstyrene (4-CMS) is rather difficult, namely direct chloromethylation of styrene yields β -chloromethyl compounds¹¹ and chloromethylation of ethylbenzene followed by bromination of the ethyl group and dehydrobromination of the product gave a mixture wherefrom it was difficult to separate the isomers¹². The same was also found by Arcus¹³ during the preparation of 4-CMS from *p*-chloromethylbenzaldehyde. By modification of the method given by G. D. Jones¹⁴ we were able to obtain the pure 4-CMS in appreciable yield. The chloromethylation of phenylethyl bromide using chloromethyl methyl ether and stannum tetrachloride resulted in formation of 4-chloromethylphenyl ethylbromide which was converted into 4-CMS using a butanol potassium hydroxyde solution. When ethanol was used instead of the higher alcohol, a hardly separable mixture of 4-CMS and 4-methyl ethyl ether was obtained.

TABLE I

Copolymerization of butadiene and 4-chloromethylstyrene in emulsion^a

Run. No.	4-CMS wt. %	Polymerization time, h	Conversion %	Copolymer		
				Cl, %	4-CMS, %	$[\eta]^b$, dl/g
P-0	0.0	18	56	0.00	0.0	1.35
P-1	30	17	63	5.76	24.6	1.54
P-2	20	20	65	4.23	18.3	1.44
P-3	15	15	52	2.86	12.3	1.74
P-4	10	16	47	2.12	9.1	1.62
P-5	7.5	12	56	0.90	3.9	1.27

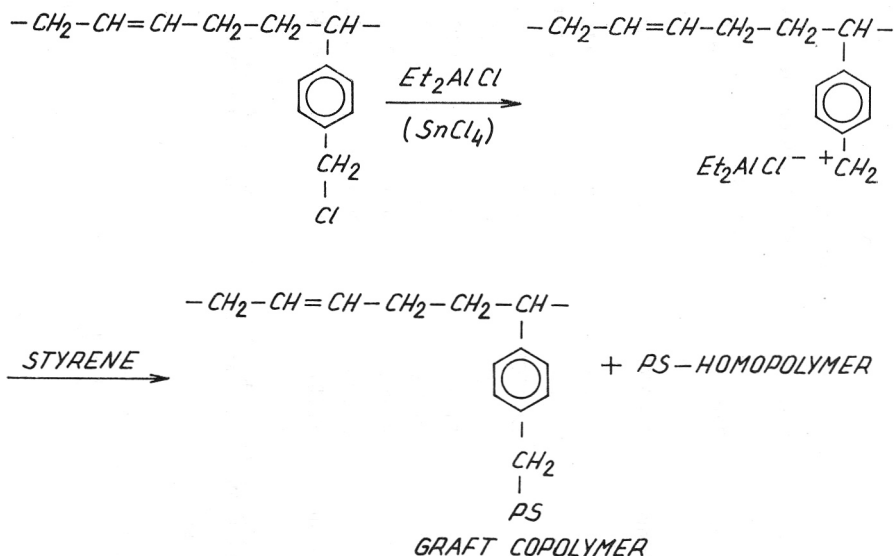
^a The polymerization was conducted at 50 °C in the presence of 0.24% $\text{K}_2\text{S}_2\text{O}_8$, 0.2% *t*-dodecylmercaptane and 10.0 g of comonomers.

^b In benzene at 30 °C.

The emulsion polymerization was terminated at about 60% conversion, yielding a random copolymer which was purified by repeated precipitation from benzene into methanol. In this way, about 20% of crosslinked material was separated. The purified copolymer was freeze-dried and used in the next step. The polymerization conditions, the compositions and the intrinsic viscosity of the copolymers are shown in Table I. Copolymers with a relative high 4-CMS content have limited shelf life due to crosslinking caused by ultraviolet light activation of the chloromethyl group and were therefore stored in dark.

Graft Copolymerization

Graft polymerization of styrene onto backbone polymer was performed in 1,2-dichloroethane as a solvent when $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ was used as a cointiator, and cyclohexane or cyclohexane-nitrobenzene mixture when SnCl_4 was used. According to the mechanism of grafting with alkylaluminums as well as with SnCl_4 , graft-initiation can occur only at chlorine sites:



where PS denotes polystyrene.

In the presence of cationogenic impurities the formation of PS-homopolymers occurs also. Therefore alkylaluminum cointiator solution was added after having established the inactivity of the initiator to the monomer in control experiments *i.e.* by attempting homopolymerization under identical conditions as used for grafting in the absence of polymeric halide.

Styrene conversion was calculated from increase in weight after drying and grafted styrene from increase in weight of the insoluble portion after extraction with boiling methyl ethyl ketone. In control experiments such treatment is quite sufficient for extracting the total homopolymers from mechanical mixtures. When polybutadiene instead of 4-CMS copolymer was used to react with styrene, in the presence of both catalyst systems, the weight after extraction with boiling methyl ethyl ketone did not increase, indicating

TABLE II
Cationic polymerization of styrene onto poly (p-chloromethylstyrene-co-butadiene)^c

Expt. No.	Elastomer ^b		Solvent	Coinitiator	Styrene Conversion, %	[η] ^c PS dl/g	Grafting %	Grafting Efficiency
	Type	Cl/%						
1.	P-0	0.0	1,2-Dichloroethane	Et ₃ AlCl	13.1	0.292	0.0	0.0
2.	P-5	0.90	"	Et ₃ AlCl	38.8	0.182	327.0	47.8
3.	P-4	2.12	"	Et ₃ AlCl	32.9	0.125	361.0	62.2
4.	P-3	2.86	"	Et ₃ AlCl	32.0	0.196	622.0	73.8
5. ^d	P-4	2.12	"	Et ₃ AlCl	15.9	0.23	196.6	42.2
6. ^e	P-4	2.12	"	Et ₃ AlCl	26.2	0.21	415.2	82.0
7.	P-4	2.12	cyclohexane	SnCl ₄	12.8	0.114	62.4	15.6
8.	P-3	2.86	"	SnCl ₄	29.3	0.16	82.9	17.2
9.	P-4	2.12	" ^f	SnCl ₄	20.3	0.122	91.5	13.2
10.	P-4	2.12	cyclohexane ^g	SnCl ₄	31.5	0.141	114.0	11.2

^a Polymerization was performed using [Coinitiator] = 1.48×10^{-2} mol/l, [Elastomer] = 3.8 g/l, [Styrene] = 0.645 mol/l, at -30°C when 1,2-dichloroethane was used and at 20°C in cyclohexane, during 2 hours.

^b The properties of the backbone polymer are shown in Table I.

^c In benzene at 30°C.

^d This experiment was performed using [Styrene] = 1.29 mole/l.

^e This experiment was performed using [Elastomer] = 5.7 g/l.

^f In the mixture of cyclohexane containing 10 vol. % of nitrobenzene.

^g In the mixture of cyclohexane containing 20 vol. % of nitrobenzene.

that no graft polymerization occurred. The percentage of grafting is defined as the ratio of the weight of grafted polystyrene to the weight of the backbone polymer used. The grafting efficiency is the ratio of grafted polystyrene to the total polystyrene obtained.

Infrared spectrum of the portion insoluble in boiling methyl ethyl ketone showed specific absorptions of both, poly(*p*-chloromethylstyrene-co-butadiene) and polystyrene, indicating that polystyrene is grafted onto the elastomer.

The polymerization conditions as well as the influence of the type of coiniciator on the grafting efficiency are summarized in Table II.

As expected, the grafting percentage and grafting efficiency increased by increasing the chlorine content in the backbone polymer used. These values also increased by higher backbone as well as styrene concentrations.

Although it is difficult to compare grafting reactions of the used initiating systems, under described conditions Et_2AlCl gave higher grafting efficiency in comparison with the results obtained when SnCl_4 was used as a coiniciator. When nitrobenzene, a polar solvent was added to cyclohexane, in the case of SnCl_4 catalised reaction, considerable higher values for grafting percentage was obtained. However, its use was limited since nitrobenzene was a nonsolvent for the backbone polymer. This result is in agreement with findings that increase polarity of the solvent promote the cationic polymerization of styrene¹⁵.

EXPERIMENTAL

Styrene, cyclohexane and nitrobenzene were purified by conventional methods.

1,2-Dichloroethane was purified by refluxing over KOH pellets and purity was checked by gas chromatography. No vinyl chloride or other impurities were found. The coiniciators, $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ or SnCl_4 were used as 10% solutions in polymerization solvents.

4-CMS was distilled from CaH_2 prior to use. The purity was established by gas chromatography.

The infrared spectra were measured with a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were determined on a Varian A-60 instrument (TMS as internal standard). Intrinsic viscosities were measured in benzene at $30 \pm 0.05^\circ\text{C}$. Melting points and boiling points are uncorrected.

p-Chloromethylstyrene

A mixture of 138.8 g (0.75 mole) of phenylethyl bromide and 161.0 g (2.0 mole) of chloromethyl ether are diluted with 350 ml of carbon disulfide and cooled to 0°C . To this solution 120 g (0.46 mole) of stannic chloride is added under stirring over a period of one hour. The reaction mixture is stirred during an additional hour and poured on ice. The solvent was removed by distillation over water respirator and the residue was distilled in vacuum yielding 76.2 g (43.5%) of the *p*-chloromethyl phenylethyl bromide, b.p. $102\text{--}103^\circ\text{C}/0.8$ mmHg. By recrystallization from ethanol a pure product melting at $49\text{--}51^\circ\text{C}$ was obtained.

A solution of 25.6 g of KOH in 280 ml of isobutanol was heated to 50°C and a solution of 70 g of *p*-chloromethyl phenylethyl bromide in 200 ml of isobutanol previously heated to 50°C was added rapidly.

The mixture was stirred 12 hours at room temperature, the precipitated KBr was filtered off and the solvent removed by distillation, the residue distilled in vacuum over a 30 cm heligrade column in the presence of di-*tert*-butyl catechole, yielding 32.3 g (10.8%) of *p*-chloromethylstyrene, b.p. $64\text{--}5^\circ\text{C}/1$ mmHg (reported¹⁴ b.p. $77.5\text{--}79^\circ\text{C}/2$ mmHg).

Anal. $\text{C}_9\text{H}_9\text{Cl}$ (152.62) calc'd.: C 70.83; H 5.94; Cl 23.23%
found: C 70.68; H 5.68; Cl 23.35%

NMR spectrum (neat) centered at: δ 4.36 (2H, chloromethyl CH_2), δ 6.21—5.67 (2H, vinyl CH_2), δ 6.66 (H, vinylidene CH), δ 7.21 (4H, ring protons).

Emulsion Polymerization

A mixture of 36 ml of a 2% aqueous solution of sodium stearate, 0.24 g of $K_2S_2O_8$, 0.1 g of *tert.* dodecylmercaptane and 1.0 g of *p*-chloromethyl styrene was placed into a 100 ml pressure bottle, which was chilled, and 9.0 g of butadiene was added, placed in a thermostated bath and kept 20 hours at 50 °C under vigorous stirring with a magnetic stirrer. The reaction mixture was poured into 250 ml of methanol and a rubbery polymer was separated, dried under vacuum, dissolved in benzene and purified by freeze-drying.

Cationic Polymerization

All polymerizations and material manipulations were carried out in a dry box under dry nitrogen. The purified and dried backbone polymer was dissolved in 1,2-dichloroethane or cyclohexane in a thermostated 50 ml round bottomed flask, equipped with a magnetic stirrer and serum cap to make a 0.5% solution. The flask was thoroughly purged with nitrogen and then styrene and the coinitiator solution were added by means of syringes. The polymerization reaction was carried out for 2 hours at -30 °C when 1,2-dichloroethane was used as a solvent and at room temperature in cyclohexane or cyclohexane-nitrobenzene mixtures. The coinitiator was destroyed by the addition of 2 ml of methanolic ammonia solution and the polymer was precipitated with 200 ml of methanol, filtered off, dried *in vacuo* and extracted 8 hours in refluxing methyl ethyl ketone.

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SAŽETAK

Kationsko cijepljenje stirena na poli (4-klorometil stiren-ko-butadien)

Z. Janović i K. Sarić

Ispitana je reakcija nastajanja cijepljenih kopolimera polimerizacijom stirena u prisutnosti poli (4-klorometil stirena-ko-butadiena) uz dietilaluminijev klorid odnosno kositreni tetraklorid kao koinicijatore u otopini 1,2-dikloretana ili cikloheksana. Klorometilirani osnovni kopolimer priređen je emulzionom polimerizacijom 4-klorometil stirena i butadiena uz $K_2S_2O_8$ kao inicijator. Promjenom odnosa monomera u početnoj smjesi, dobiveni su kopolimeri sa određenim sadržajem prisutnog klora.

Povećan sadržaj cijepljenog kopolimera dobiven je upotrebom $AlEt_2Cl$ kao koinicijatora kao i također kod većeg sadržaja klora u osnovnom polimeru.