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Synthesis of Poly(Indene-*g*-Isobutylene) by Cationic Techniques

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Summary

Poly(indene-g-isobutylene) was prepared by cationic graft copolymerization of isobutylene from halogenated polyindene. Product analyses suggest a grafting from mechanism.

Introduction

The use of indene as comonomer in graft copolymerizations was described by numerous authors. However, in most of the papers concerning cationic techniques for graft copolymer synthesis polyindene was the pendant polymer chain. SIGWALT et al. (1976 a-c) and BAUDIN et al. (1980) used chlorobutyl rubber, chlorinated ethylene propylene copolymers and 1,4-cis polybutadiene as well as EPDM as backbones in graft copolymerizations with indene. PARY et al. (1978) reported on the synthesis of poly(isobutylene-co-p-chloromethylstyrene-g-indene) by cationic techniques. The use of polyindene as backbone has been described so far only for radical processes. RUAULT and MARECHAL (1970) used diazotized polyindene in conjunction with $FeSO_4$ as radical initiator for grafting from copolymerizations of vinyl acetate, styrene, methyl methacrylate and acrylo nitrile.
The aim of this paper is to describe a cationic route for the synthesis of graft copolymers with polyindene backbones. Furthermore, it will be shown that a grafting from mechanism is likely.

Experimental

Materials: Commercial indene (99 %) was purified by the usual methods and distilled twice under dry argon atmosphere from CaH_2 and immediately used for polymerizations. Isobutylene was dried over Na/K alloy and condensed in baked out storage vessels. CH_2Cl_2, CCl_4 and chlorobenzene were purified by conventional methods and distilled twice each from P_2O_5 and CaH_2 under dry argon. $TiCl_4$ was distilled under dry argon from copper powder and P_2O_5 subsequently. $AlEt_2Cl$ was used as a 10 % solution in pure heptane. N-Bromo-succinimide (NBS) preparation followed a recipe by HORNER and WINKELMANN (1959). N-Chlorosuccinimide (NCS) was prepared according to TSCHERNIAK (1901).

Polymerizations: All polymerizations and graft copolymerizations were carried out in specially designed baked out glass reactors under dry argon atmosphere. The preparation of polyindenes was described earlier (HOTZEL et al. 1982). For graft copolymerizations the reactor was charged with solvent, macroinitiator (chlorinated or brominated polyindene) and comonomer (isobutylene). The mixtures were stirred at 195 K using a Dry Ice/methanol bath. The polymerizations were then started by direct introduction of the coinitiator solution. After one hour the reactions were terminated by the addition of a few ml of methanol. The resulting materials were precipitated into methanol and reprecipitated twice from benzene/methanol (1:5). Fractionation of graft copolymers was carried out by precipitation of benzene solutions of the materials into heptane and ethyl methyl ketone (MEK). The products were characterized by GPC, VPO, ^1H-NMR and IR-spectroscopy.

Macroinitiators: Brominated polyindenes ($PInBr_n$) were prepared by the conversion of polyindene (PIn) with NBS in CCl_4 at 75 °C. Chlorinated polyindenes ($PInCl_n$) were prepared by the reaction of PIn with NCS in chlorobenzene at 132 °C.

Both radical initiators such as dibenzoyl peroxide (DBPO) and UV-light were additionally applied. After 4-5 hours the reaction mixtures were cooled to room temperature, filtered and precipitated into methanol. The materials were dissolved in benzene and washed with aqueous $NaHSO_3$ and subsequently several times with bidistilled water. Then the solutions were dried over Na_2SO_4, precipitated into methanol and repricipitated from benzene/methanol (1:5). The resulting materials were dried in vacuo at room temperature for at least three days.

Results and Discussion

TABLE I shows the results of the macroinitiator preparations. With increasing concentration of NBS and NCS respectively the halide content in the polymer does increase too. However, the halide content of $PInX_n$ is always below the value expected for a 100 % conversion of the halogenating reagents. Furthermore, the comparatively mild reaction conditions during the bromination with NBS do only lead to negligible chain degradation whereas the higher extent of chain degradation during chlorination by NCS is probably due to the elevated temperature. The use of DBPO does not improve the results of chlorination. Reaction under UV-irradiation leads to a slight increase in chlorine content, however, severe chain degradation takes place. Products of dark brown color were obtained in these cases. Best results yields the use of NCS or NBS alone. The much higher UV-absorbance of the halogenated products compared with the starting materials at 254 nm (UV-detector response in GPC-investigations) hints the presence of double bonds in the backbone as it could be approximately calculated from the iodine numbers (compare column 6 in TABLE III).

TABLE II shows the results of grafting experiments using the halogenated polyindenes as initiators in conjunction with $AlEt_2Cl$ as coinitiator of cationic isobutylene polymerization. All products are 100 % soluble in heptane. This indicates a complete conversion of the $PInX_n$ macroinitiators because polyindene is insoluble in heptane. The presence of a MEK soluble and a MEK insoluble fraction in the crude products, however, hints chemical inhomogeneity of the materials as it can also be concluded from the GPC-elution diagrams (compare FIGURE 1). The MEK soluble fractions are white powders of low molecular weight and low isobutylene content. The MEK insoluble fractions are yellowish till brown elastomeric materials of higher molecular weight and high isobutylene content (compare columns 4 and 5 in TABLE III). Polyisobutylenes eventually formed during graft copolymerizations could not be separated by fractionation. The comparison of UV- and IR-detector responses in double detection GPC analyses, however, suggest that the MEK insoluble fraction is a homogeneous material.

The ratio of MEK soluble and MEK insoluble fractions depends on the relative amounts of PIn and IB in the feeds of graft copolymerizations and the conversion of IB. At similar PIn/IB ratios the $PInCl_n$ initiators yield a higher IB conversion than the $PInBr_n$ initiators. This is in agreement with the observations by KENNEDY et al. (1973) that chlorides are more effective initiators of cationic polymerizations than bromides in conjunction with aluminium alkyl coinitiators.

TABLE I: Results of Bromination and Chlorination of PIn with NBS and NCS respectively

Nr.	reaction conditions				results	
	PIn/g	M_n(VPO)	NCS/g	remarks	M_n(VPO)	% halide
reactions with NBS in CCl_4 at 75 °C						
(1)	5.0	9500	2.0	-	8650	4.8 (Br)
(2)	5.0	9500	1.5	-	8800	4.0 (Br)
(3)	5.0	9500	0,95	-	10500	3.1 (Br)
(4)	5.1	4000	1.6	-	3000	3.7 (Br)
reactions with NCS in chlorobenzene at 132 °C						
(5)	5.8	9000	3.6	-	7100	6.0 (Cl)
(6)	5.8	9000	3.6	0.1g DBPO	7350	3.1 (Cl)
(7)	5.8	9000	3.6	UV-light	3250	6.7 (Cl)
(8)	14.5	5700	8.7	-	4300	7.7 (Cl)

TABLE II: Results of Cationic Graft Copolymerizations of Isobutylene from Halogenated Polyindene at 195 K Using Et_2AlCl as Coinitiator, in CH_2Cl_2, 1 Hour Reaction Time

Nr.	$PInX_n$/g a)	IB/g	CH_2Cl_2 ml	$AlEt_2Cl$ ml	Conv. %IB	% MEK. sol.	% MEK insol.
B1	2.9 (1)	8.7	100	0,5	58.6	8.0	92.0
B2	4.85 (4)	10.0	150	1.5	70.1	41.2	58.8
C1	3.0 (5)	9.0	100	0,5	68.3	9.1	90.9
C2	2.5 (8)	1.2	100	0,7	82.9	n.d.	n.d.
C3	7.0 (8)	14.0	200	0.54	100.0	12.7	87.3

$AlEt_2Cl$ as 10 % solution in heptane

a) ... compare TABLE I

TABLE III: Characterization of selected Products of Grafting Experiments in TABLE II

Nr.	material	% halide	M_n (VPO)	mole % IB (NMR)	n. DB a)
B1	$PInBr_n$	3.67	3000	o	n.d.
	crude product	0.16	8900	n.d.	n.d.
	MEK-sol.	n.d.	7400	62.0	n.d.
	MEK-insol.	n.d.	20000	79.0	n.d.
C3	$PInCl_n$	7.66	4300	0	10.0
	crude product	1	n.d.	n.d.	n.d.
	MEK-sol.	1.66	3900	55.0	n.d.
	MEK-insol.	1	12900	83.0	12.0

a) n. DB ... number of double bonds calculated from iodine numbers

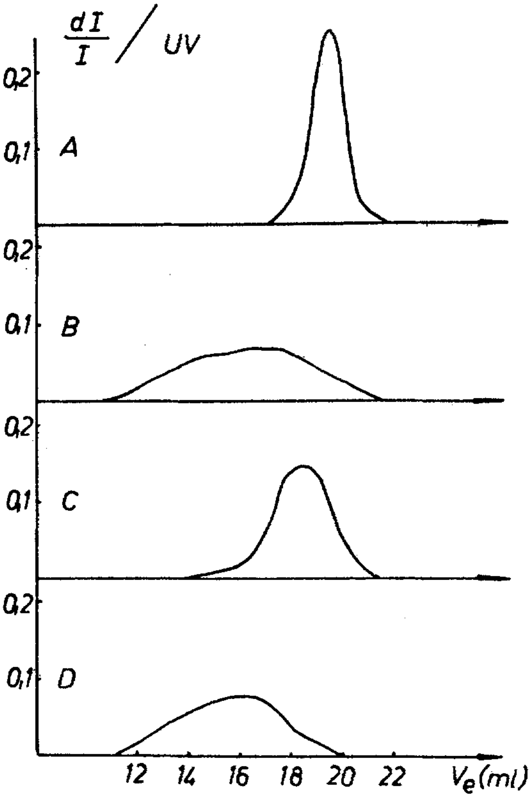

FIGURE 1:

GPC-Elution Diagrams of C 3 in TABLE III

A... $PInCl_n$ (starting material)

B... Crude Product of Grafting Experiments

C... MEK Soluble Fraction

D... MEK Insoluble Fraction

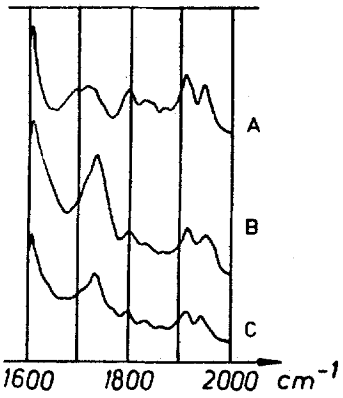

FIGURE 2:

IR-spectra of C 3 in TABLE III

A... PIn

B... $PInCl_n$

C... P(In-g-IB), MEK soluble fraction

The mechanism of cationic graft copolymerizations using aluminium alkyl coinitiators has been subject of a controversy between different schools. KENNEDY has provided strong evidence for a grafting from mechanism with the halogenated backbone polymer as initiator (compare KENNEDY and MAREÇHAL 1982). Other authors claim a grafting onto mechanism with carbenium ion termini of growing chains attacking double bonds in the backbone. In this case the initiation is supposed to occur as a result of direct interaction between alkyl aluminium halides and the comonomer (compare GANDINI and CHERADAME 1980).

The results reported in this paper strongly support KENNEDY's theory. First of all, growing carbenium ions should not only attack double bonds in the backbone but also alkylate aromatic rings. The IR-spectra, however, show no evidence of trisubstituted aromatic rings in the polymer whereas normal 1,2-disubstitution of indene structures is present (compare FIGURE 2). Second, the halide content of the graft copolymers is close to zero (compare column 3 in TABLE III), i.e. all C-halogen bonds were ionized during the interaction with $AlEt_2Cl$. Third, the numbers of double bonds in the polymer remain constant during graft copolymerization within the confidence intervall of the experimental method (compare column 6 in TABLE III). Whereas double bonds are introduced during chlorination of PIn by NCS (probably by HCl elimination as a side reaction) there is no significant difference between $PInCl_n$ and the graft copolymer.

Though the formation of polyisobutylene could not be excluded by fractionation experiments the results presented here can be considered as additional arguments in favour of a grafting from route (compare KENNEDY and WONDRACZEK 1982).

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