

New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers)

11. Synthesis, Extension and Crosslinking of Oxycarbonyl Isocyanate Telechelic Polyisobutylenes

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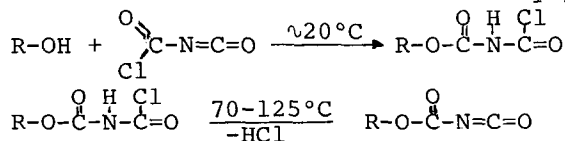
Summary

Novel oxycarbonyl isocyanate telechelic polyisobutylenes have been prepared by conversion of hydroxyl-terminated polyisobutylenes with N-chlorocarbonyl isocyanate. This reaction is free from side-reactions and provides highly reactive isocyanate-terminated polyisobutylene prepolymers. Conversion of these prepolymers with glycol, urea, pentaerythritol, and polyethylene glycol led to linear chain extension, crosslinking, and multiblock copolymer formation, respectively.

Introduction

Previous papers in this series of publications concerned the synthesis of a new family of telechelic polyisobutylenes (KENNEDY and SMITH, 1980a, KENNEDY et al. 1979, KENNEDY et al. 1981, IVAN et al. 1980) their derivatization (KENNEDY et al. 1979, KENNEDY et al. 1981, IVAN et al. 1980) and their use for the preparation of sequential block copolymers (KENNEDY and SMITH 1980b). In a separate publication we described the synthesis of novel Nylon-6-Polyisobutylene-Nylon-6 tri-blocks starting with the telechelic polyisobutylene diol HOCH₂-PIB-CH₂OH (WONDRAKZEK and KENNEDY, 1980). The latter synthesis involved the conversion of this diol with toluene diisocyanate (TDI) to telechelic polyisobutylene diisocyanates OCN-PIB-NCO and inducing the anionic polymerization of ε-caprolactam. The reaction between HOCH₂-PIB-CH₂OH and TDI, however, has been found to be accompanied by a small but consistent measure of undesirable chain extension.

We theorized that this side-reaction could be avoided by the use of N-chlorocarbonyl isocyanate, ClCO-NCO, (NCCI) instead of TDI since according to HAGEMANN (1977) the conversion of alcohols with NCCI can proceed in the absence of unwanted by-products:



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This chemistry has been described and exploited by a British (1970) and a German patent (1974) which disclose the conversion of organic hydroxyl compounds with NCCI to oxycarbonyl isocyanates $-\text{OCO}-\text{NCO}$.

An advantage of the $-\text{OCO}-\text{NCO}$ end group is that it is more reactive in isocyanate reactions than $-\text{C}_6\text{H}_4-\text{NCO}$ or $\{\text{CH}_2\}_n\text{NCO}$ termini.

It occurred to us that the conversion of $\text{HOCH}_2-\text{PIB}-\text{CH}_2\text{OH}$ by NCCI to oxycarbonyl isocyanate telechelic polyisobutylenes $\text{OCN}-\text{CO}-\text{O}-\text{PIB}-\text{O}-\text{CO}-\text{NCO}$ would be of greatest interest for the synthesis of a large variety of potentially useful macromolecules. This paper concerns synthesis and initial derivatization experiments with $\text{OCN}-\text{CO}-\text{O}-\text{PIB}-\text{O}-\text{CO}-\text{NCO}$ and various $-\text{OH}$ and $-\text{NH}_2$ containing compounds i.e., glycol, urea, pentaerythritol (Pe) and polyethylene glycol (PEG). Our research with $\text{OCN}-\text{CO}-\text{O}-\text{PIB}-\text{O}-\text{CO}-\text{NCO}$ for the preparation of PIB/Nylon-6 block copolymers will be reported separately (WONDRACZEK, KENNEDY 1981).

Experimental

Synthesis of $\text{HOCH}_2-\text{PIB}-\text{CH}_2\text{OH}$

The preparation of hydroxyl telechelic polyisobutylene $\text{HOCH}_2-\text{PIB}-\text{CH}_2\text{OH}$ has been described (KENNEDY and SMITH 1980a) KENNEDY et al. 1979, IVAN et al. 1981) together with the analytical method used for the determination of OH-group concentration (WONDRACZEK and KENNEDY 1981). The average end group functionality \bar{F}_n (OH) of the prepolymer used in this research cannot be less than 1.95. The \bar{M}_n of the diol was 6,000 and $\bar{M}_w/\bar{M}_n = 1.70$.

Synthesis of $\text{OCN}-\text{CO}-\text{O}-\text{PIB}-\text{O}-\text{PIB}-\text{O}-\text{CO}-\text{NCO}$

Experiments were carried out under a dry nitrogen atmosphere in baked-out 250 ml three-necked flasks equipped with stirrer, soxhlet extractor with solvent withdrawer (ACE) filled with molecular sieves (3A, Fisher) to exclude moisture. The $\text{HOCH}_2-\text{PIB}-\text{CH}_2\text{OH}$ was dissolved (40 wt %) in decaline (Baker, dried with Na/K alloy) and a four fold excess of benzene (dried with Na/K alloy) was added. Decaline was omitted for derivatizations carried out in bulk (see Table I). One third of the benzene was distilled off for azeotropic drying of the charge. The solution was cooled to $0-5^\circ\text{C}$, a five fold excess of N-chlorocarbonyl isocyanate, NCCI, (Aldrich) relative to HO- was added, and the system was stirred for 2 hrs at $0-5^\circ\text{C}$ and 6 hours at room temperature. Subsequently the benzene and excess NCCI were distilled off. The heating of the system also effected dehydrochlorination of the intermediary adduct formed between $\text{HOCH}_2-\text{PIB}-\text{CH}_2\text{OH}$ and NCCI. The HCl evolved was removed by a steady stream of N_2 passing through the system and was monitored by precipitation of AgCl from a AgNO_3 solution. The product, $\text{OCN}-\text{CO}-\text{O}-\text{PIB}-\text{O}-\text{CO}-\text{NCO}$ in decaline solution or in bulk (see

above) was used in further derivatizations.

The -NCO content was quantitatively determined by benzylation with benzyl alcohol followed by UV spectroscopy. Details of this analytical method will be reported (WONDRACZEK and KENNEDY 1981). According to the analysis of representative samples $\bar{F}_n(-OH)$ and $\bar{F}_n(-NCO)$ were virtually identical which indicates quantitative conversion of the -OH to the -O-CO-NCO function.

Reactions of OCN-CO-O-PIB-O-CO-NCO with Functional Compounds

These experiments were carried out using 250 ml three necked flasks equipped with mechanical stirrer under a blanket of dry (molecular sieves, 3A, Fisher) nitrogen. The charges consisted of 7.6g of PIB(-O-CO-NCO) and equimolar amounts of glycol, urea, pentaerythritol (Pe) and polyethylene glycol (PEG) of $\bar{M}_n = 1,000$. The four latter compounds are commercially available (Aldrich) and have been used after drying under vacuum over P_2O_5 (urea and Pe), with molecular sieves (glycol), and in the form of a THF solution over molecular sieves (PEG). Three series of experiments were carried out: 1) in decaline solution (40 wt %), 2) in bulk, and 3) in bulk in the presence of di-tert. butyl tin laureate (0.1 wt %) (see Table I). The PIB(-OC-O-NCO)₂ either in bulk or in decaline solution was stirred at 140°C and the reagents were introduced. Solid reagents (urea and Pe) were added via a Schlenk tube under anhydrous conditions, the glycol was added by a syringe, and the PEG in a 50% THF solution by a syringe (the THF was immediately purged out by the nitrogen stream at 140°C). The charges in decaline solutions were stirred for 24 hours whereas those in bulk until the increase in viscosity prevented further stirring. The charges turned increasingly yellow with progressing reaction. The mixtures with urea became noticeably hazy after about five hours. The reactions were stopped by cooling the charges to room temperature.

The products obtained in bulk experiments were purified by adding to the charges toluene (50 ml), filtering, and precipitating into acetone. Products of experiments in which decaline solutions were used were precipitated directly into acetone. Subsequently the products were dissolved in benzene and repeatedly reprecipitated into methanol (1:10) and dried in vacuo until weight constancy at 60°C (~five days). Yield and conversion data in Table I have been obtained with the purified products.

The products were characterized by GPC (Waters instrument with differential refractometer, Model R401 and UV absorbance detector, Model 440, THF solutions, series of 7 Styragel columns) using PIB calibration and

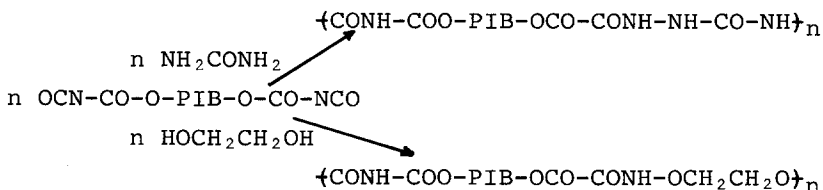
$^1\text{H-NMR}$ spectroscopy (Varian T60, 10 wt.% solutions in deuterated DMSO).

The results of visual observations are included in Table I. All products were yellowish except those made with glycol which were colorless.

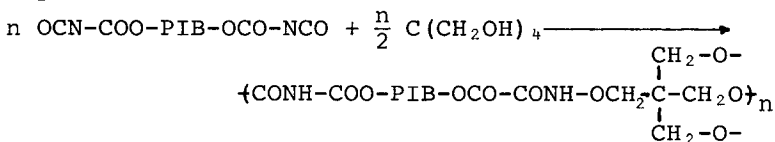
Results and Discussion

Results of chain extension with urea and glycol, crosslinking with pentaerythritol (Pe), and multi-blocking with polyethylene glycol (PEG) are shown in Table I. The exact conversions are probably higher than those given in Table I because material losses during purification are unavoidable.

Conversion of oxycarbonyl isocyanate telechelic polyisobutylene with the bifunctional reagents urea and glycol leads to linear chain extension:



Polyfunctional reagents lead to crosslinking, for example with Pe:



Side-reactions of the highly reactive oxycarbonyl isocyanate groups, particularly with impurities such as traces of moisture are possible but not the subject of these investigations.

Extension and crosslinking numbers n obtained in reactions carried out by the use of decaline solutions were consistently lower than those obtained in bulk. The use of di-*tert*-butyltin laureate catalyst showed only a marginal effect. Reactions in the absence of catalyst in decaline and in bulk were quite slow as indicated by the fact that the gel point has not been reached even with the tetrafunctional reagent Pe.

GPC analyses of the THF soluble products from the reactions with Pe showed bimolecular distributions of which the main peak has been used to calculate the \bar{M}_n 's shown in Table I. The minor peak ($\sim 5\%$ of the total) appeared at elution volumes close to the upper exclusion limit indicating a very high molecular weight component ($\bar{M}_n \gg 100,000$)

The conversion of $\text{PIB}(-\text{OCO-NCO})_2$ with PEG yields block copolymers $(\text{PIB-PEG})_n$:

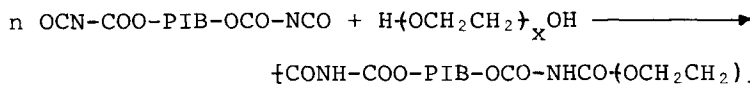


Table II shows compositions and extension numbers n of (PIB-PEG) $_n$ block copolymers calculated from $^1\text{H-NMR}$ analyses.ⁿ

Table II: Composition and Extension Numbers (n) Calculated from $^1\text{H-NMR}$ Analyses of (PIB-PEG) $_n$

System	IB mole%	PEG mole%	$n(\text{PIB})$	$n(\text{PEG})$
decaline solution	83	17	1.91	2.60
bulk	87.8	12.2	6.05	5.60
bulk, catalyst	87.2	12.8	7.02	6.85

Although the GPC analyses were carried out by the use of PIB calibration curves the extension numbers show excellent agreement (compare data in Table I and II). Again, the reactions in bulk yielded higher extension numbers than those carried out in solution; the catalyst had very little effect on n .

These preliminary studies demonstrate the suitability of oxycarbonyl isocyanate terminated polyisobutylenes for further macromolecular syntheses. The extremely reactive oxycarbonyl isocyanate termini yield more reactive prepolymers than those obtained with aliphatic or aromatic isocyanate groups. These materials hold promise for chain extensions, cross-linking, and for the synthesis of A-B and (AB) $_n$ block copolymers.

Acknowledgement

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References

- BRITISH PATENT B.P. 1,226,277 (1970)
 HAGEMANN, H.: German Patent DOS 2,300,541 (1974)
 HAGEMANN, H.: Angew. Chemie 89, 789 (1977)
 IVAN, B., J. P. KENNEDY and V.S.C. CHANG: J. Polym. Sci.-Chem. Ed. 18, 3177 (1980)
 KENNEDY, J. P., V.S.C. CHANG, R. A. SMITH and B. IVAN: Polym. Bull. 1, 575 (1979)
 KENNEDY, J. P. and R. A. SMITH: J. Polym. Sci.-Chem. Ed. 18, 1523 (1980a)
 KENNEDY, J. P. and R. A. SMITH: J. Polym. Sci.-Chem. Ed. 18, 1539 (1980b)
 KENNEDY, J. P., L. R. ROSS, J. E. LACKEY and O. NUYKEN: Polymer Bull. 4, 67 (1981)
 WONDRACZEK, R. H. and J. P. KENNEDY: Polymer Bull. 2, 675 (1980)
 WONDRACZEK, R.H. and J. P. KENNEDY: to be published, 1981

Table I: Results of Reactions of PIB(NCO)₂ with Functional Reagents

Reaction	Yield g	Conversion %	\bar{M}_n^* $\times 10^{-3}$	\bar{M}_w/\bar{M}_n	n extension number**	Visual Observation
<u>Reactions in Decaline Solution</u>						
Urea	6.76	89	25	1.57	4.2	viscous liquid (honey)
Glycol	6.46	85	27	1.65	4.5	viscous liquid (honey)
Pe	6.92	91	49	2.63	8.2	highly viscous liquid
PEG	7.45	81	14	1.53	2.0	viscous liquid (honey)
<u>Reactions in Bulk</u>						
Urea	6.47	85	45	1.85	7.5	sticky rubbery
Glycol	6.31	83	61	2.00	10.2	sticky rubbery
Pe	6.23	82	92	2.75	15.3	tacky rubbery
PEG	6.72	73	45	2.00	6.4	sticky rubbery
<u>Reactions in Bulk with Catalyst</u>						
Urea	6.61	87	47	1.94	7.8	sticky rubbery
Glycol	6.77	89	76	2.13	12.7	sticky rubbery
Pe		toluene insoluble gel, no data available				
PEG	6.44	70	50	2.14	7.1	sticky rubbery

Abbreviation: Pe = pentaerythritol, PEG = polyethylene glycol

*estimated by GPC using PIB calibration

**number of chain extensions for urea and glycol, number of crosslinked chains for Pe, and n for (PIB-PEG)_n block copolymers