Macromol. Symp. ***127****, 109–114 (1998)*

POLYFUNCTIONAL POLYISOBUTENES AS BUILDING BLOCKS FOR AMPHIPHILIC GRAFT POLYMERS

Martin Grasmüller, Juan C. Rueda-Sanchez, Brigitte I. Voit, Oskar Nuyken*

Lehrstuhl für Makromolekulare Stoffe, Technische Universität München
Lichtenbergstrasse 4, 85747 Garching (Germany)

Abstract: Polyfunctional polyisobutenes (PIB) have been synthesized by cationic copolymerization of isobutene and chloromethylstyrene. Their potential applications with focus on their use as macroinitiators (**MI**) for oxazoline polymerization were discussed. The „grafting from" reaction led to tailor-made graft copolymers with various backbones and adjustable graft arm length. Graft copolymers with hydrophobic PIB backbone and poly(2-methyloxazoline) graft arms have unusual viscosity properties due to their amphiphilic character and show aggregate formation.

INTRODUCTION

PIB, which is prepared by cationic polymerization, is an inexpensive hydrophobic petro polymer and is resistant against most chemicals (Ref.1). It is a very gas-tight elastomer and exhibits excellent damping properties Therefore, the incorporation of functional PIB blocks into other polymeric materials is of great interest.

Many PIB block and graft copolymers have been prepared by various research groups (Ref.2). The required functionalities are often introduced by polymeranalogous modification of the backbone or the end groups in a multistep procedure. An easier approach to backbone modified PIB is the copolymerization of isobutene with functionalized monomers that allow cationic polymerization.

SYNTHESIS OF POLYFUNCTIONAL POLYISOBUTENES

We used the copolymerization of isobutene (**IB**) and chloromethylstyrene (**CMS**) as a one-step-approach to polyfunctional PIB (Ref. 3,4). The product is slightly branched since CMS can act as well as monomer and as initiator. The polymerizations were carried out in methylene chloride with BCl_3 or $TiCl_4$ as coinitiator. The number of benzyl chloride groups was adjustable by stoichiometry. Some examples of macroinitiators (**MI**) are listed in Table 1. Homo-poly(chloromethylstyrene)

CCC 1022-1360/98/$ 10.00

(poly(CMS)) was prepared via free radical polymerization and was used as highly functional linear reference macroinitiator.

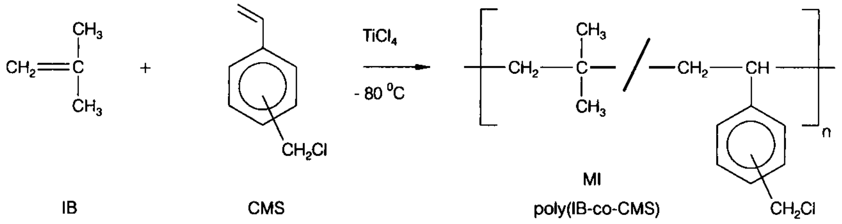

Fig. 1: Synthesis of macroinitiators

Table 1: Synthesis and properties of macroinitiators **MI** (Ref. 5)

MI	Coinitiator (CI)	$[CI]_0$/ [CMS]0	M_n g/mol	Ar-CH_2Cl mol%
MI1a[1]	BCl_3	0.2	7,400	58
MI1b[1]	$TiCl_4$	0.1	16,300	27
MI2[2]	(AIBN)		21,200	100

[1] MI1: CH_2Cl_2, -80 °C

[2] MI2: bulk, 70 °C, free radical polymerization

APPLICATION SPECTRUM FOR POLYFUNCTIONAL PIB

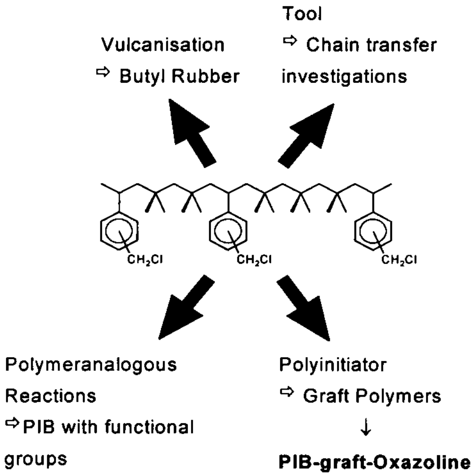

Fig. 2: Potential applications of polyfunctional PIB

The copolymers of isobutene and chloromethylstyrene have a broad application spectrum. Their vulcanization with diamines leads to butyl rubber (Ref.3) and polymeranalogous reaction of the versatile benzyl chloride groups allows the introduction of other functional groups.

However, the most obvious potential is their use as macroinitiators. Benzyl chloride groups are known as initiator functions for a number of cationically polymerizable monomers, e.g. isobutene (Ref. 4), styrene (Ref. 6) and oxazolines (Ref. 7). In addition, the grafting reaction can be an important tool in order to study chain transfer. „Grafting from“ with a second monomer M_2 can lead to graft copolymer PIB-*graft*-M_2 and to M_2-homopolymer. The amount of homopolymer is proportional to chain transfer and to initiation from non-polymeric sites. When no homopolymer is formed then there is obviously no chain transfer and no initiation by impurities (e. g. water). We used polyfunctional polyisobutenes as macroinitiator for grafting reactions with various oxazolines and no homo-polyoxazoline was formed in any case.

GRAFT COPOLYMERS WITH OXAZOLINES

SYNTHESIS

The properties of polyoxazolines vary from hydrophilic (e.g. poly(2-methyloxazoline)) to hydrophobic (e. g. poly(2-nonyloxazoline)). This allows to tailor their surface activity and leads to potential applications as compatibilizers in blends. They are used also as precursors for linear poly(ethyleneimine). Polyoxazolines are prepared by ring-opening cationic polymerization.

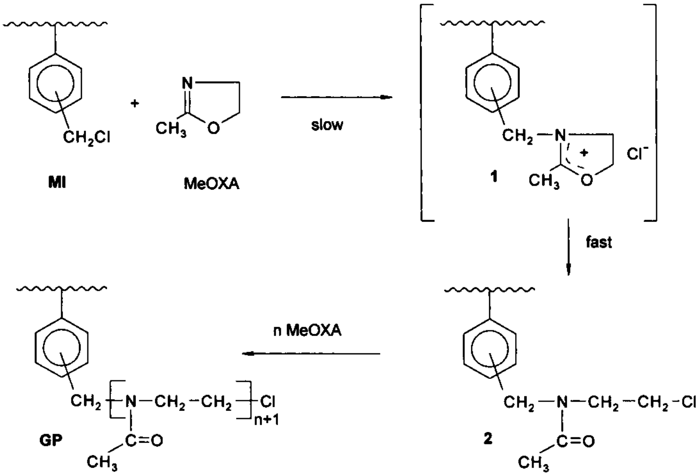

Fig. 3: Grafting of oxazolines from benzyl chloride groups

Graft copolymers PIB-*graft*-(2-methyloxazoline) were prepared in benzonitrile solution at 110 °C according to Fig.3. The cationic polymerization of oxazoline by the covalent mechanism, which is proposed for the system initiated with a benzyl chloride group (Ref.7), is slow and only about 40 % conversion of MeOXA were achieved after 48 h reaction time. The addition of KI to the polymerization shifts the equilibrium towards the more reactive ionic oxazolinium species **1** (Fig. 3) and accelerates the polymerization strongly. This effect was studied in detail for the grafting reaction with nonyl- and phenyloxazoline (Ref.8). The graft arm length could be controlled by reaction time and thus, by conversion. Table 2 summarizes some results for the MeOXA graft reaction.

Table 2: Graft copolymerization with 2-methyloxazoline (MeOXA)

graft copolymer GP	macroinitiator MI	conv. MeOXA in %	P_n graft arm calc.
GP1	**MI1a**	38	6
GP2	**MI1a**	40	46
GP3	**MI2**	53	34
GP4	**MI1a**	17	7
GP5	**MI1a**	21	17
GP6	**MI1b**	38	10

The amphiphilic character of the graft copolymers could be tailored by the polarity of the oxazoline graft monomer. The graft copolymers from 2-phenyloxazolines are soluble in acetonitrile but not in ethyl acetate or toluene which are solvents for the macroinitiators. Poly-PIB-*graft*-(2-nonyloxazoline)s are soluble in toluene but not in ethyl acetate or diethyl ether. The graft copolymers with MeOXA are soluble in chloroform, in methanol, and in pure water.

PROPERTIES

The strong amphiphilic character of the graft copolymers with MeOXA shows clearly in their solution behavior. The graft copolymers are soluble in water **and** in chloroform. In the proton NMR in $CDCl_3$ the signals of the backbone and the graft arms can be detected while in D_2O only the signals of the graft arms are visible. This indicates that in water the unpolar PIB-backbone collapses to a core and is shielded by the polar MeOXA-graft arms.

In addition, dynamic light scattering experiments in water proved also the formation of aggregates since the determined hydrodynamic radii R_h of 40 nm are much larger than those expected for single molecules.

This leads to unusual viscosity properties. Measurements in chloroform (Fig. 4) as well as in methanol showed very low viscosities for all graft copolymers. The viscosities were in all cases below those observed for the ungrafted macroinitiators. The slightly branched structure of **MI1** is demonstrated in the fact that the viscosity of **MI1** is much lower than that of the linear poly(CMS) of similar molar mass. In addition, the plots of reduced viscosity (η_{sp} / c) versus the concentration were approximately a constant function for the graft copolymers, whereas the macroinitiators showed an increase in viscosity with increasing concentration. This viscosity behavior is typical for polymeric solutions in which the macromolecules are fully collapsed or form aggregates.

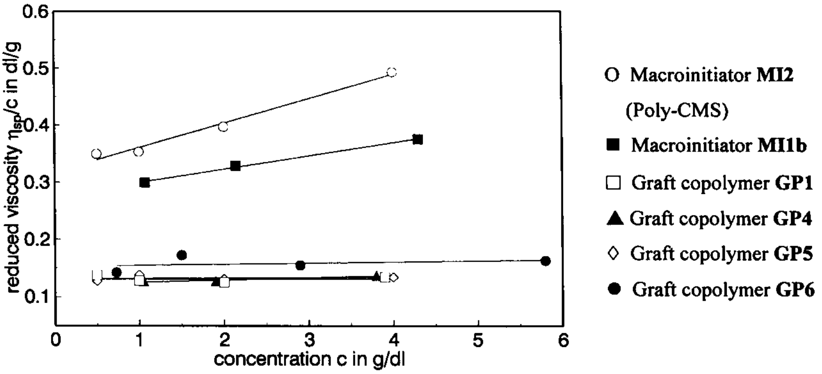

Fig. 4: Reduced viscosities of macroinitiators and graft copolymers (**GP**)

It is interesting to note that a very similar viscosity behavior was found for **GP1** to **GP6** also in water and, again, when the temperature of the measurement was increased to 60 °C, indicating the formation of very stable aggregates.

First tests on the application of these amphiphilic graft copolymers as primer in adhesive technology as well as compatibilizer in blends already proved the high potential of these products.

ACKNOWLEDGMENTS

The authors would like to thank the German Academic Exchange Service (DAAD) for a research fellowship of Juan Rueda-Sanchez and BAYER for financial support of Martin Grasmüller.

REFERENCES

(1) K. P. Meurer, „Polymere mit C-Hauptketten durch Polymerisation von Isoolefinen bzw. Olefinen mit endständiger Doppelbindung“, in: *Houben-Weyl, Methoden der organischen Chemie*, 4th ed., Vol. E20/2, H. Bartl, J. Falbe, Eds., Thieme Verlag, Stuttgart 1987, p. 770

(2) J. P. Kennedy, E. Marechal, „*Carbocationic Polymerization*“, Wiley Interscience Publishers, New York 1982, p. 409 ff

(3) G. D. Jones, J. R. Runyon, J. Ong, *J. Appl. Polym. Sci.* **5**, 452 (1961)

(4) O. Nuyken, F. Gruber, S. Pask, A. Riederer, M. Walter, Makromol. Chem. 194, 3415 (1993)

(5) O. Nuyken, J. Rueda-Sanchez, B. I. Voit, *Macromol. Rapid Comm.* **18**, 125 (1997)

(6) J. P. Kennedy, „*Cationic Polymerization of Olefins: A Critical Inventory*", Wiley Interscience Publishers, New York 1975, p. 234

(7) T. Saegusa, S. Kobayashi, A. Yamada, *Makromol. Chem.* **177**, 2271 (1976)

(8) O. Nuyken, J. Rueda-Sanchez, B. I. Voit, *Polym. Bull.* **38**, 657 (1997)