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SYNTHESIS OF POLY(STYRENE-CO-BUTADIENE-g-ISOBUTYLENE) AND POLY(STYRENE-CO-ISOPRENE-g-ISOBUTYLENE) VIA A COMBINED RADICAL/CATIONIC ROUTE

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ABSTRACT

A synthetic route for graftcopolymers with macroinitiators synthesized by free radical polymerization in emulsion and polyisobutylene side arms is described. Unsaturated macroinitiators can be obtained by copolymerization of dienes with styrene and a styrene-based derivatives. The resulting macroinitiators poly(styrene-co-2-acetoxy-2-(4-vinylphenyl) propane-co-butadiene) and poly(styrene-co-2-acetoxy-2-(4-vinylphenyl)-propane-co-isoprene) were used to initiate the cationic homopolymerization of isobutylene. The macroinitiators and the graftcopolymers were characterised with common methods such as NMR, IR and GPC.

INTRODUCTION

The polymerization of isobutylene and its copolymerization with isoprene are processes of great technical importance [1]. Both processes are characterized by their sensitivity towards impurities and the danger of side reactions at higher temperatures. Therefore, the homo- and the

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*Corresponding author. Fax: +49 89 289 13562; E-mail: oskar.nuyken@ch.tum.de copolymerization are carried out at temperatures close to $-100°C$. Moreover, only small concentrations of isoprene are tolerated for a certain level of molecular masses of the desired copolymers. Common copolymers of isobutylene/isoprene do not contain more than 2–5 mol% of isoprene.

In common copolymers each chain must contain a certain level of unsaturation for the subsequent vulcanization and must reach a rather high molecular mass to fulfill application requirements. An alternative strategy one could follow is grafting from using macroinitiators [2–8]. Then it is not necessary that each chain reaches a high molecular mass but the sum of the masses of all side arms of the resulting graftcopolymer leads to high molecular mass polymers.

The advantage of this strategy includes not only the possibility of shortening the branches but also the gain in flexibility of the design of the macroinitiator. In a former paper we described the synthesis of the poly(styrene-g-isobutylene-co-isoprene) containing unsaturated side arms [9]. An extended strategy, that will be described in this contribution deals with the synthesis of new macroinitiators that contain C,C-double bonds in the backbone. These macroinitiators were synthesized via emulsion polymerization.

EXPERIMENTAL

All chemicals, if not otherwise indicated, were received from Aldrich and were used without further treatment. Styrene was purified removing the inhibitor by a basic aluminium oxide column followed by distillation. Isobutylene (Linde) was passed through a column with molecular sieves and through a column with potassium on aluminium oxide. Methylenchloride was dried over $CaH_2{\cdot}BCl_3$ was received from Merck.

Monomer synthesis: The synthesis of 2-acetoxy-2-(4-vinylphenyl)propane (<u>4</u>) has been described in the literature [9].

Polymerization: Emulsion copolymerization of styrene, <u>4</u> and the dienes was done in an autoclave at $+10°C$. About 20 g of monomers were emulsified with 0, 5 g sodium dodecylsulfate. Initiation at these low

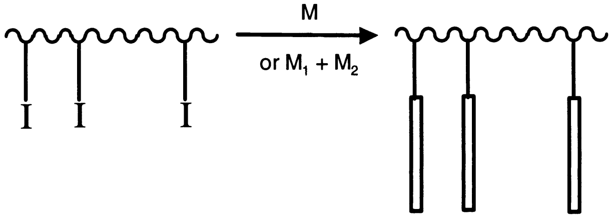


Figure 1. Polymers with high molecular mass via multifunctional macroinitiators.

temperatures was performed with a redox system consisting of 20 or 40 mg ^{t}BuOOH as initiator, 4 mg $FeSO_4 \cdot 7H_2O$, 6 mg ethylenediaminetetraacetate (EDTA) and 25 mg sodium formaldehydsulfoxylate (Rongalit$^{\circledR}$) buffered with 1,0 g $Na_2HPO_4 \cdot 2H_2O$. Dodecylmercaptane was used as regulator. The polymer is dissolved in CH_2Cl_2 and precipitated in MeOH. This procedure was repeated for three times. The macroinitiators were dried for 3 days in fine vacuum over molecular sieves (3, 4 and 5 Å) to remove water and methanol.

^{1}H-NMR ($CDCl_3$): δ(ppm) 7,3-6,5 (aromatic), 5,6-5,0 (olefinic) 2,7-1,0 (aliphatic) IR (KBr): (cm^{-1}) 3025 (Ar-H), 2922 ($-CH_3$, $-CH_2-$), 1736 (C=O), 1601 (Ar), 1493 (Ar), 1452 (Ar-H), 967 (Ar), 757 (Ar), 697 (Ar).

Graft copolymerization of isobutylene was carried out in a MBraun Glovebox under argon atmosphere. The process temperature was $-80°C$. The reaction was started by the addition of pre-chilled BCl_3 and stopped after 60 minutes by the addition of 3 mL pre-chilled methanol.

Synthesis of the Macroinitiator

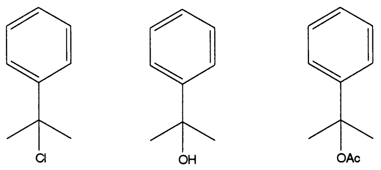
It is known that cumylchloride (1), 2-hydroxy-2-phenyl-propane (2) and 2-acetoxy-2-phenylpropane (3) can be used as initiators for the cationic polymerization of isobutylene [9].

Typical initators for the cationic polymerization of isobutylene: cumyl chloride (1), 2-hydroxy-2-(4-vinylphenyl)-propane (2), 2-acetoxy-2-(4-vinylphenyl)-propane (3).

Macroinitiators with X = Cl have been synthesized earlier by an anionic copolymerization of α-methylstyrene with 1,4-diisopropenylbenzene followed by HCl addition to the pendant olefinic groups [11]. The anionic route is limited due to the selectivity of the initiating species towards monomers.

Table 1. Copolymerization of Styrene 4 and Butadiene or Isoprene via Emulsion Polymerization

	Monomers			Polymerization		Product	
Macroinitiator	Styrene [g]	4 [g]	Diene [g]	Regulator [mg]	Initiator [mg]	Yield [%]	Gel [%]
P1	16,8	1,2	0,7	28	40	41	7
P2	2,5	1,0	20,0	14	20	16	20
P3	12,2	2,7	8,7	14	40	16	14
P4	16,8	1,1	1,9	28	40	58	2
P5		1,4	8,2	14	20	27	46



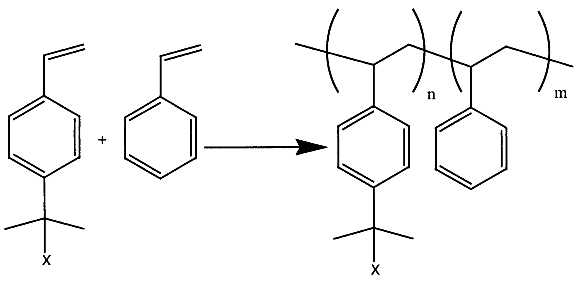
1 **2** **3**

Figure 2. Typical initiators for the cationic polymerization of isobutylene: cumyl chloride (1), 2-hydroxy-2-(4-vinylphenyl)-propane (2), 2-acetoxy-2-(4-vinylphenyl)-propane (3).

More attractive than the anionic route is the radical route due to its great flexibility concerning the design of the backbone. A detailed synthesis for X = OAc has been described [9]. A polymer analogous reaction was presented in the literature [12]. Radical copolymerization of styrene and 4 in solution initiated by AIBN resulted in macroinitiators without any unsaturation. The desired unsaturation was introduced in the final graft copolymers via graft copolymerization of isobutylene and isoprene. The extended concept is now to introduce the unsaturation into the macroinitiator via radical terpolymerization of styrene, butadiene (or isoprene) and 4. The method of choice for such a terpolymerization is the emulsion polymerization because of the incorporation of butadiene or isoprene in the backbone, which is easier in emulsion then in other techniques.

It is well known that radical copolymerization allows the incorporation of any amount of butadiene into the polymer. Macroinitiators with low amounts of butadiene are white powders, while the ones with a higher amount of butadiene are elastic materials. The incorporation of isoprene into the polymer is also possible.

A series of macroinitiators with different diene content was prepared. The content of 4 was kept around 3 mol%. High molecular masses could be obtained. The yield was not optimized because dienes tend to form insoluble



(4): X = OAc

Figure 3. Synthesis of macroinitiators by radical copolymerization of styrene and styrene based derivatives.

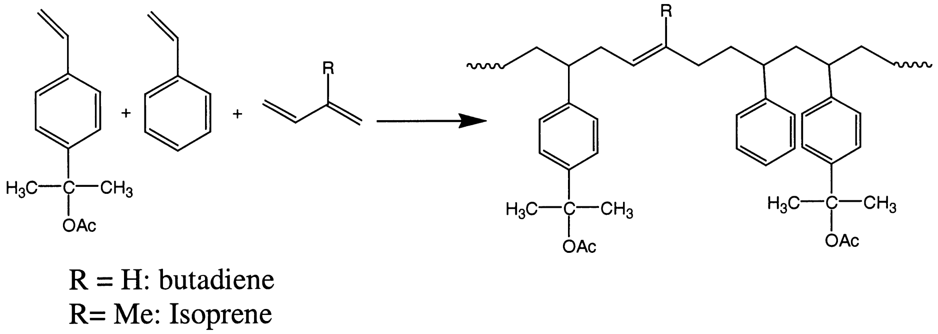


Figure 4. Synthesis of a macroinitiator with C=C double bonds in the backbone by terpolymerization of styrene, 4 and a diene by emulsion polymerization.

crosslinked polymers when conversion is to high. Therefore, in technical applications the polymerization is stopped at a yield of 60% [13].

Graft Copolymerization with Isobutylene

The macroinitiators were dissolved in dichloromethane and cooled to −80°C. Then the desired amount of isobutylene was added. Grafting was started with prechilled BCl_3 dissolved in CH_2Cl_2.

Low reaction temperature is necessary to reduce transfer reactions. The macroinitiator itself was completely converted into graft copolymers, meaning that no unreacted macroinitiator was detectable. Unfortunately, it

Table 2. Copolymers of Styrene 4 and Butadiene or Isoprene via Emulsion Polymerization (The Polymers Were Analyzed with H-NMR and GPC)

Macroinitiator	Styrene[1] [mol%]	4[1] [mol%]	Diene[1] [mol%]	M_n[2] [g/mol]	M_w[2] [g/mol]	N_4[3] [ ]
P1	88,8	3,2	8,0[4]	60.000	152.00	19
P2	7,5	1,5	91,0[5]	93.000	293.000	23
P3	33,8	3,8	62,5[5]	49.000	143.000	24
P4	75,4	2,6	22,0[5]	51.000	335.000	14
P5	–	5,0	95,0[5]	41.000	121.000	33

[1] Calculated from ^{1}H-NMR.
[2] Determined by GPC.
[3] Number of 4 in the polymer, calculated from GPC and 1 H-NMR. Only 4 can initiate the cationic graftpolymerization.
[4] Diene = Isoprene.
[5] Diene = Butadiene.

Table 3. Grafting Experiments, Initiating System Poly(St-co-4-co-diene)/Bcl$_3$/CH$_2$Cl$_2$/ T = −80°C

Macroinitiator			Graft Product			
Diene	Amount of Diene [%]	M_n [g/mol]	M_n [g/mol]	M_w [g/mol]	Gel [Weight%]	Graft Efficiency [%][1]
Isoprene	8	60.000	159.000	1.154.000	0	55
Butadiene	22	51.000	232.000	1.145.000	0	40
Butadiene	63	49.000	180.000	596.000	35	45
Butadiene	91	73.000	–[2]	–[2]	60	–[2]
Butadiene[3]	95	41.000	–[2]	–[2]	50	–[2]

[1] Graft efficiency is defined as the ratio of graftcopolymer to the sum of graftcopolymer plus homopolyisobutylene.

[2] The graftproduct is completely unsoluble. Therefore, no results are presented. The obtained product is the homopolyisobutylene, which is the result of transfer reactions.

[3] The macroinitiator contains 95% of butadiene and 5% of 4 but does not contain any styrene.

was not possible to avoid the formation of homopolyisobutylene completely. However, the validity of the concept is shown by a strong increase of molecular masses. This strategy allows the synthesis of graft copolymers containing C,C-double bonds in the backbone and having a molecular mass higher than $M_w = 1.000.000$ g/mol.

In principal the degree of unsaturation in the macroinitiator is unlimited. However, with increasing amounts of butadiene or isoprene the danger of gelation of the graftcopolymers increases due to the fact that the C,C-double bonds of the backbone are not inert towards the growing carbocations.

The relationship between the amount of diene and the molecular masses, the graft efficiency and the network formation is depicted in Fig. 5.

From this picture one can clearly see, that it is advantageous to start graftcopolymerization with macroinitators containing only low amounts of unsaturation. The graft efficiency does not depend on the amount of unsaturation. In order to reduce the danger of network formation the level of unsaturation should not be higher than 20%. The molecular mass of the graftproducts seems to decrease with increasing amounts of diene in the macroinitiator. This can be understood if one takes into account that the high molecular mass fractions are insoluble due to network formation and therefore only the soluble parts of the polymers can be determined by GPC. Graftcopolymers with low amounts of diene are completely soluble. The resulting GPC curves are trimodal. A low molecular mass fraction belongs to the homopolyisobutylene, that is RI active but UV inactive. Since the high molecular mass fractions are RI and UV active, these fractions are two types

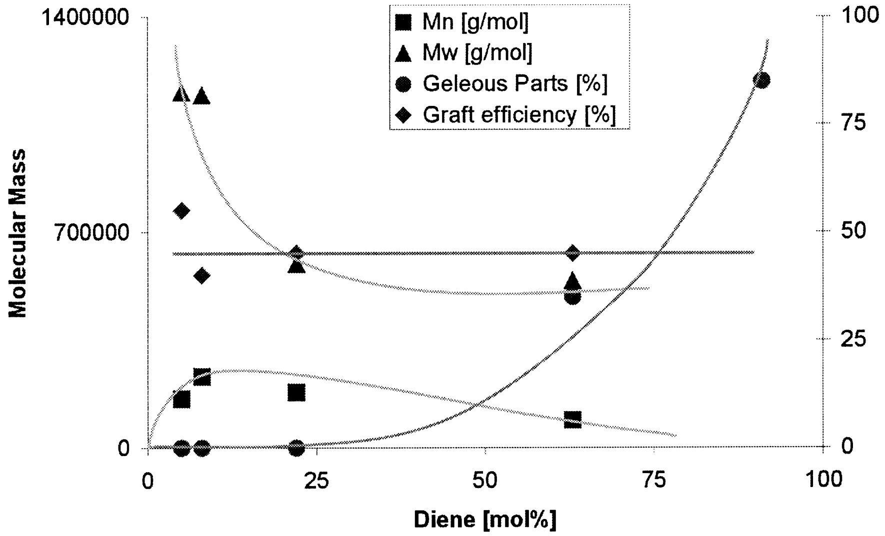


Figure 5. Relationship between the amount of diene and the molecular mass, the graft efficiency and the network formation.

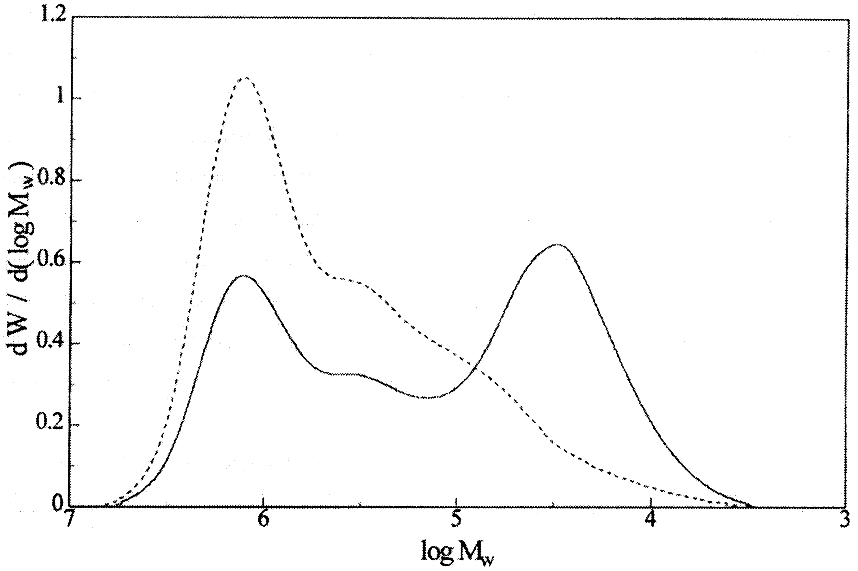


Figure 6. Trimodale distribution of the product. The dashed line belongs to the UV canal, the other line to the RI canal.

of graftcopolymer. The medium mass fraction belongs to the graftpolymer. The highest fraction belongs to a graftcopolymer that was attacked by a growing chain, but remains soluble.

CONCLUSION

The work presented in this article opens attractive routes for the synthesis of high molecular graftcopolymers by combination of different polymerization techniques. The strategy described here allows a flexible design of different macroinitiators (type and number of comonomers, number of initiating groups, etc.). This concept was applied to a graftcopolymer, having a poly(styrene-co-diene) backbone and polyisobutylene side arms. Emulsion polymerization was applied to the macroinitiator synthesis since it is the method of choice for the terpolymerization of styrene, 2-acetoxy-2-(4-vinylphenyl)propane and butadiene. The resulting polymers are effective initiators for the cationic polymerization of isobutylene. The polyisobutylene side arms were synthesized via cationic polymerization at −80°C initiated by BCl_3. If the amount of diene in the backbone is lower than 20% the resulting graftcopolymers are completely soluble having a molecular mass average around 1.000.000 g/mol. Therefore, this concept allows the synthesis of high molecular polyisobutylenes containing sufficient unsaturated units in the backbone for common applications. Since many parameters can be varied, this concept is attractive and extremely flexible, allowing the design of a great variety of polymer structures.

ACKNOWLEDGMENT

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REFERENCES

1. Duffy, J.; Wilson, G.J. Synthesis of Butyl Rubber by Cationic Polymerization, Ullmann's Encyclopedia of Industrial Chemistry, 5. Aufl. Elvers; Hawkins, S.; Russey, W.; Schulz, G., Hrsg., VCH Verlagsgesellschaft mbH, Weinheim. **1993**, *A23*, 288.
2. Gadkari, A.; Kennedy, J.P. J. Appl. Polym. Sci. Appl. Poly. Symp. 44 (Int. Semin. Elastomers), **1989**, 19.
3. Puskas, J.E.; Grasmüller M. Macromol. Symp., 132 (International Symposium on IonicPolymerization, 1997), **1998**, 117.
4. Donderer, M. Diploma Thesis, TU München, **1993**.
5. Donderer, M. Ph.D. Thesis, TU München, **1996**.

6. Grasmüller, M. Diploma Thesis, TU München, **1995**.
7. Kennedy, J.P.; Keszler, B.; Fenyvesi G. US Pat. 6228945, 15. CA 2001:331324, 2001.
8. Kennedy, J.P.; Ivan, B. *Designed Polymers by Carbocationic Macromolecular Engineering, Theory and Practice*; Carl Hanser Verlag: Munich, Vienna, New York, Barcelona, 1991; 219.
9. Donderer, M.; Langstein, G.; Schäfer, M.; Nuyken, O. Submitted to Polymer Bulletin.
10. Kennedy, J.P.; Ivan, B. *Designed Polymers by Carbocationic Macromolecular Engineering, Theory and Practice*; Carl Hanswer Verlag: Munic, Vienna, New York, Barcelona, 1991; 16.
11. Mühlbauer, H.P.; Nuyken, O. 9th Int. Symp. on Cationic Polymerizations and Related Ionic Processes, Strasbourg, France, June 5–9, 1989.
12. Frechet, J.M.J. US Pat. 5084522, 1992, CA 1326045, 1988.
13. Logemann, W. Methoden der Organischen Chemie, Houben-Weyl, 4 Aufl. Bd. 14/1.Müller, E., Hrsg. Themie Verlage: Stuttgart, 1961, 468.

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