Polymer Bulletin 47, 509-516 (2002)

Polymer Bulletin

A combined radical/cationic synthetic route for poly(styrene-g-isobutylene) and poly(styrene-g-isobutylene-co-isoprene)

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Received: 30 July 2001/ Revised version:3 December 2001/ Accepted: 3 December 2001

Summary

A synthetic route for graftcopolymers, in which the poly(styrene-co-2-acetoxy-2-(4-vinylphenyl)propane) was synthesized via a radical pathway is described. The resulting macroinitiator was used to initiate the cationic homopolymerization of isobutylene and the cationic copolymerization of isobutylene with isoprene. The resulting polymers were characterised with common methods such as $^{1}H/^{13}C$-NMR, IR and GPC.

Introduction

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

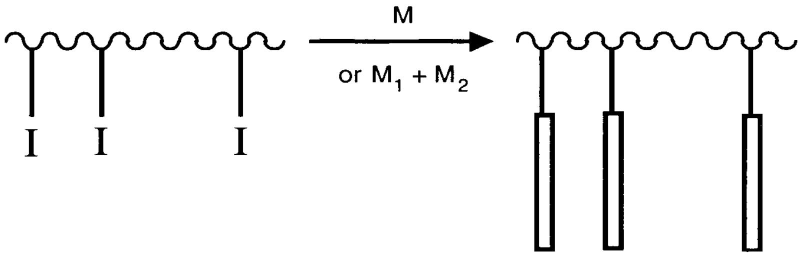


Figure 1. Polymers with high molecular mass via multifunctional macroinitiators

via macroinitiators [2-7,8a]. In this case it is not necessary that each chain reach a high molecular mass but the sum of all side arms of the resulting graftcopolymer.
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. On the other hand one has to consider that the macroinitiator can change the properties of the obtained rubber or lead to microphase separation.

Experimental

All chemicals - if not otherwise indicated – were received from Aldrich and 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. AIBN was recrystallized twice from methanol. Dichloromethane was dried over $CaH_{2,}$ hexane was dried over potassium. BCl_3 was received from Merck.

Monomer synthesis:

2-Hydroxy-2-(4-vinylphenyl)-propane (4): 36.31 g (0.20 mol) *para*-bromostyrene in 100 ml tetrahydrofurane (THF) was added dropwise into 4.86 g (0.20 mol) magnesium in 100 ml THF. After 2 hours refluxing 17.42 g (0.30 mol) acetone in 100 ml THF was added slowly. After 2 hours the mixture was cooled to 0 °C and hydrolyzed by 20.0 g ammonia chloride in 100 ml distilled water. After the addition of 100 ml THF the organic phase was separated and dried with magnesium sulfate. The raw product was purified by distillation. The yield was 76 %.
^{1}H-NMR ($CDC1_3$): δ (ppm) 7,45-7,20 (aromatic); 6,68 (aromatic); 5,71 (olefinic); 5,20 (olefinic); 1,53 (aliphatic)
IR (KBr): δ,ν (cm^{-1}) 3415 (HO-), 3085 (H-C=C), 2975 (H_3C-), 2930 (H_3C-), 1630 (C=C), 1510 (C=C), 1465 (C=C), 1365 (H_3C-), 1170 (C-O), 990 (H-C=C), 905 (H-C=C), 840 (C-H)
2-Acetoxy-2-(4-vinylphenyl)-propane (5): 1.22 g (0.01 mol) 4-N,N-dimethylamino-pyridine were added to 24.33 g (0.15 mol) 4 in 100 ml triethylamine. After stirring for 15 minutes 22.97 g (0.23 mol) acetic anhydride was added. The mixture was stirred for 24 hours at room temperature. Then, 200 ml ether was added, the organic phase was separated, dried and purified by column chromatography (hexane:acetic anhydride 15:1). The yield was 92.5 %.
^{1}H-NMR ($CDCl_3$): δ (ppm) 7,45-7,20 (aromatic); 6,68 (aromatic); 5,71 (olefinic); 5,20 (olefinic); 2,01 (aliphatic); 1,74 (aliphatic)
IR (KBr): δ,ν (cm^{-1}) 3085 (H-C=C), 2980 (H_3C-), 2935 (H_3C-), 1630 (C=C), 1740 (C=O); 1630 (C=C); 1515 (C=C), 1470 (C=C), 1365 (H_3C-), 1245 (C-O), 990 (H-C=C), 910 (H-C=C), 840 (C-H)

Polymerization:

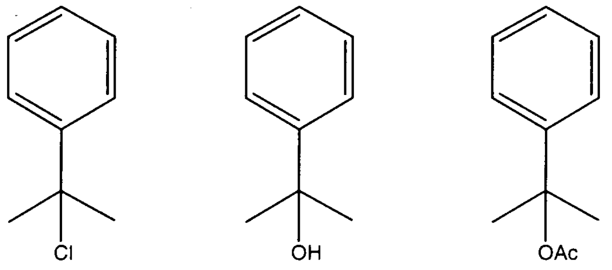
Radical copolymerization of styrene and 5 was carried out in toluene by 60 °C using AIBN as initiator. For the determination of the copolymerization parameters the overall monomer concentration was 25 mmol and the conversion was always kept below 5 %. Therefore, the reaction time varied between 40 and 600 minutes.

Otherwise the reaction time was 48 hours. Graftcopolymerizations were studied in a MBraun Glovebox under argon atmosphere at –80 °C. The grafting reaction was started by the addition of prechilled BCl_3 and stopped after 60 minutes by the addition of 3 ml prechilled methanol.

The copolymerization parameters were determined by use of ^{1}H-NMR and IR spectroscopy.

Synthesis of the macroinitiator

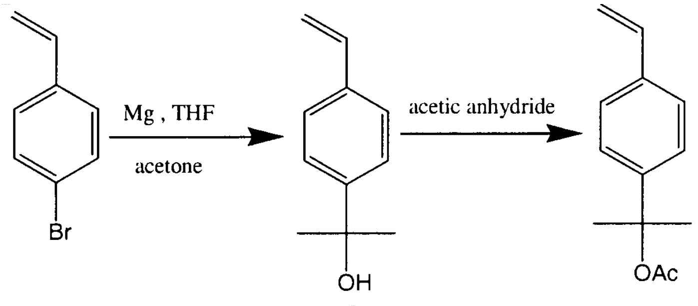
It is known that cumylchloride (1), 2-hydroxy-2-phenyl-propane (2) and 2-acetoxy-2-phenylpropane (3) can be used as initiator for the cationic polymerization of isobutylene [8b]. Their incorporation into a polymer chain is possible via different routes [9,10]. The anionic route is limited due to the selectivity of the initiating species. However, we were able to show that this method is suitable for the synthesis of macroinitiators. More attractive than the anionic route is the radical route due to its great flexibility concerning the design of the backbone.



1 2 3

Figure 2. 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).

A detailed synthesis for 5 will be described. A polymer analogous reaction is presented in the literature [11]. We decided to synthesize the corresponding monomer according to the following scheme:



4 5

Figure 3. Synthesis of 2-acetoxy-2-(4-vinylphenyl)propane (5) by a Grignard reaction followed by an esterification.

4-Bromo-styrene was reacted with magnesium and the resulting Grignard reagent was converted into 4 by reaction with acetone. The reaction of 4 with acetic anhydride results in the unsaturated initiator 5.

Radical copolymerization of 5 with styrene was carried out in different ratios of the monomers. The results are depicted in Figure 4. As one can see from the results almost any ratio styrene/5 can be realized. Moreover, the copolymerization parameters r_1 = 0,97 and r_2 = 0,98, determined by the method of Mayo-Lewis [12] and Fineman-Ross [13] indicate almost ideal copolymerization behaviour.

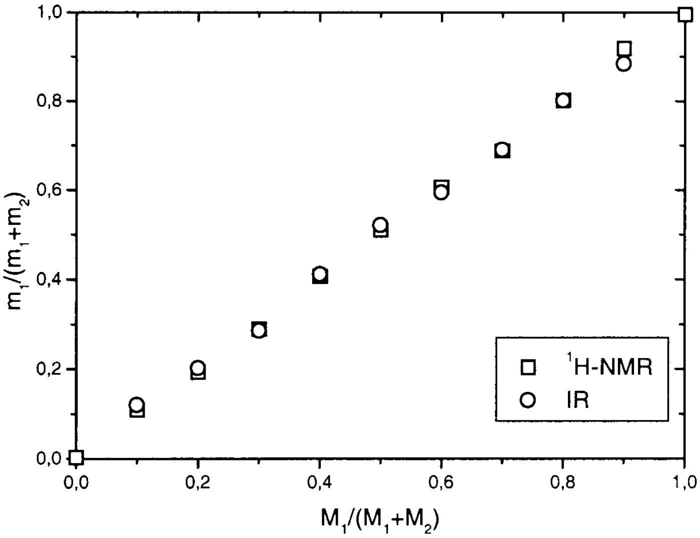


Figure 4. Radical copolymerization of styrene (M_1) and 5 (M_2) in toluene at 60 °C initiated with AIBN. The polymerization was quenched by a conversion lower than 5 %. = ^{1}H-NMR (O-CO-CH_3 at 2,02 ppm), O = IR (ν(C=O) at 1740 cm^{-1} and $\delta(C_6H_5)$ at 700 cm^{-1}).

Therefore, the starting monomer mixtures could be converted into polymers up to 100 % conversion without changing their chemical composition. The polymers were analysed by quantitative ^{1}H-NMR (O-CO-CH_3 at 2,02 ppm) and quantitative IR (ν(C=O) at 1740 cm^{-1} and $\delta(C_6H_5)$ at 700 cm^{-1}). The molecular masses were determined by GPC calibrated with polystyrene standards. The results are summarised in Table 1.

Table 1. Copolymerization of styrene and 5 in toluene initiated with AIBN at 60 °C. The resulting polymers were analyzed with ^{1}H-NMR and GPC.

Styrene$^{(1)}$ [mol%]	**5$^{(1)}$ [mol%]**	**$M_n^{(2)}$ [g/mol]**	**PDI**	**$N_5^{(3)}$**
94,6	5,4	63100	1,81	31
90,3	9,7	54800	1,65	47
79,2	20,8	48100	1,65	80
66,9	33,1	62600	1,82	151
49,3	50,7	58300	1,81	191

(1) Calculated from ^{1}H-NMR
(2) Determined by GPC
(3) Number of initiating units for each polymer, calculated by 1H-NMR and GPC

As one can see the molecular mass does not depend on the chemical composition. The number of initiating units is controllable by the monomer composition.

Graftcopolymerization 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.

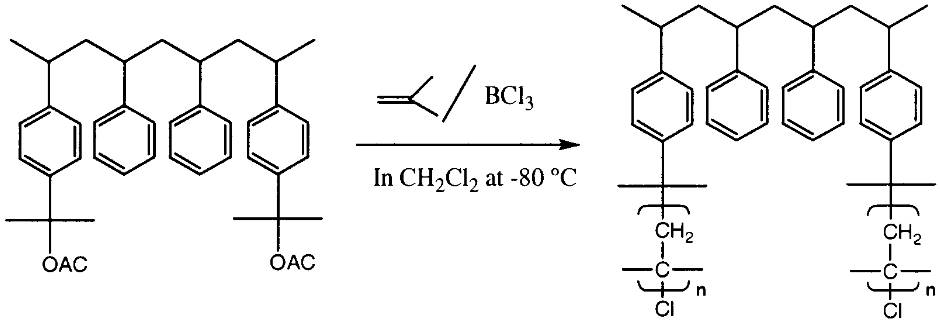
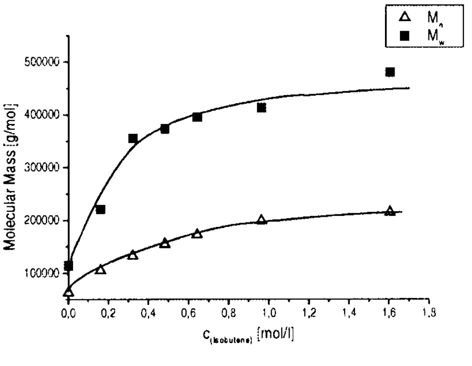


Figure 5. Graftcopolymerization of poly(styrene-co-2-acetoxy-2-(4-vinylphenyl)-propane) with isobutylene in dichloromethane at –80 °C initiated by BCl_3.

In a typical experiment 100 mg macroinitiator was reacted with 2150 mg isobutylene, which was converted completely into graftcopolymers. The GPC curves show a strong increase of molecular mass. The low temperature was necessary to avoid transfer reactions. However, since the curves are monomodal in UV but bimodal in RI detection one must conclude that it was not possible to avoid the formation of homopolyisobutylene completely. The macroinitiator itself was completely converted into graftcopolymers, meaning that no unreacted macroinitiator was detectable.



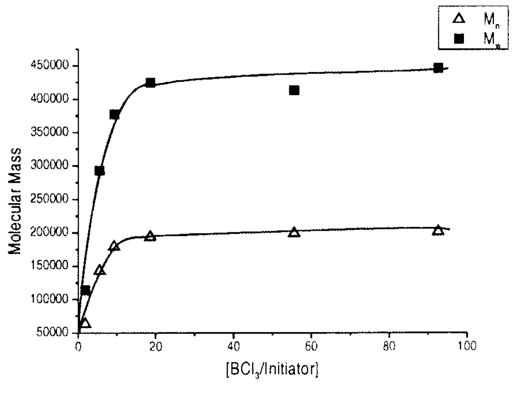


Figure 6. Relation between molecular mass and isobutylene concentration.

Figure 7. Relation between molecular mass and the ratio of coinitiator to initiator.

1,5 µmol macroinitiator (M_n = 63100 g/mol); 6,4 mmol to 64 mmol isobutylene; 2,5 mmol BCl_3 (figure 6); 0,2 mmol to 4,5 mmol BCl_3; 38 mmol isobutylene (figure 7); 40 ml CH_2Cl_2; T = - 80 °C; t = 60 min.

The molecular masses are controlled by the ratio of macroinitiator to monomer, the higher the amount of monomer the higher the molecular mass of the product. At high amounts of monomer an upper limit of molecular mass is reached. This could probably be explained by assuming that at this limit every side arm is inactive due to transfer reaction. Therefore, only homopolymer is produced after that time.

From the graph one can see that it is possible to reach suitable levels of molecular masses due to the multiarm growing. It is also interesting to note that the molecular mass also depends on the amount of the coinitiator BCl_3 due to partial initiation. At a 10 to 20 fold excess of BCl_3 over initiating units a plateau of molecular masses is reached. This means that for an effective initiation an excess of BCl_3 is needed.

The molecular masses were determined by GPC calibrated with polystyrene standards. Therefore, and because of the lower hydrodynamic volume of graftcopolymers, the values given in the figures and tables are even underestimated.

Graftcopolymerization with isobutylene and isoprene

For technical applications it is of interest to synthesize polymers that contain double bonds. In a series of experiments the macroinitiators were applied for the initiation of isoprene and isobutylene/isoprene mixtures. Finally isobutylene and isoprene were added stepwise.

Table 2. Grafting experiments, Initiating system Poly(St-co-5): M_n=63100 g/mol, M_w=113900 g/mol; 2,5 mmol BCl_3; 40 ml CH_2Cl_2; T=-80 °C

Experiment	Isobutylene [mol/l]	Isoprene [mol/l]	M_n [g/mol]	M_w [g/mol]
1	0,962	---	200800	427100
2	---	0,962	165000	410300
3 (1)	0,962	0,096	179800	415900
4 (2)	0,962	0,096	217300	483700

(1) Premixture of isobutylene and isoprene
(2) Addition of isoprene after 60 min

Similar recipes were used for the synthesis of these graftcopolymers as for the graftcopolymers with polyisobutylene side arms. The products were characterised by ^{1}H-NMR and GPC, the data are summarized in Table 2. It could be shown that the macroinitiator is able to initiate the homopolymerization of isoprene and the copolymerization of the mixtures. The copolymerization of isobutylene and isoprene leads to statistical copolymers. The sequential addition leads rather to a gradient polymer than a blockcopolymer, due to incomplete conversion of isobutylene.

The products are of high molecular mass so they could fit for common applications. Surprisingly, no gelation of the products was observed. This is due to the fact that all side arms are initiating the cationic polymerization. Each arm itself is short and has a low degree of unsaturation in case of isobutylene/isoprene copolymerization. Therefore, no gelation of the products can be observed. The influence of isoprene as a transfer agent [14] is also very small in this case.

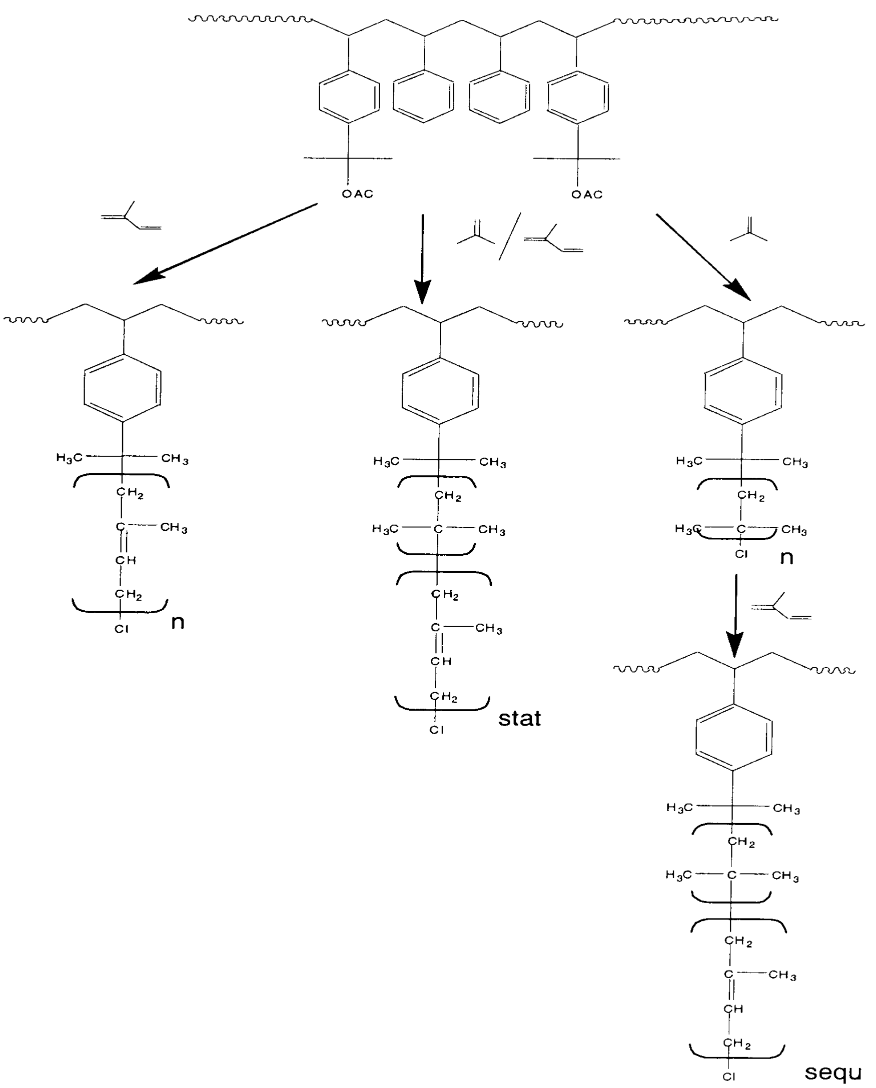


Figure 8. Graftcopolymerization with isoprene, isobutylene/isoprene mixtures and sequential addition of the monomers. The macroinitiator is dissolved in CH_2Cl_2, cooled to – 80 °C. Polymerization is started by the addition of prechilled BCl_3.

Conclusion

The work presented here opens attractive routes for the synthesis of graftcopolymers by combination of different polymerization techniques. The applied strategy allows the design of different macroinitiators (monomers, number of initiating groups, etc.). This concept was successfully used for the synthesis of graftcopolymers, having a polystyrene backbone and polyisobutylene or poly(isobutylene-co-isoprene) side arms. In other words radical copolymerization was applied for the macroinitiator synthesis and then the side arms were synthesized via cationic polymerization. Many parameters can be varied. Therefore, this concept is attractive and flexible, allowing the design of a great variety of polymer structures.

Acknowledgements. Financial support of the Bayer AG is gratefully acknowledged. M. Schäfer wants to thank the Konrad-Adenauer-Stiftung for grant.

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