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Mechanical and Dynamic Properties

Guayule Rubber Centered Block Copolymers

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SUMMARY

A synthesis concept has been developed for selective cleavage of cis-1,4-poly(isoprene) - guayule or natural rubber - with synchroneous functionalization, conversion of the telechelics to bifunctional macroinitiators and subsequent polymerization of the hard blocks. Thermoreversibly crosslinked poly(methylmethacrylate)-(b-cis1,4-poly(isoprene)) threeblock copolymers synthesized in this way have been characterized, and mechanical properties have been measured.

In parallel α, ω - poly(isobutylene) diols capable to form bifunctional macroinitiators have been synthesized.

INTRODUCTION

Guayule rubber is an alternative for natural rubber earned from Hevea Brasiliensis. Guayule - Parthenium Argentatum - is a bush which is growing naturally in the wilderness, in Northern Mexico and in Texas. Even if the expenditure for the isolation of the cis-1,4-poly(isoprene) is prohibitive up to now, the guayule bush may offer a valuable regrowing polymer in future.

Thermoplastically processable threeblock or starblock copolymers are an attractive class of macromolecular systems, because good processibility and high niveau of applicational properties are combined. Insertion of regrowing macromolecules into such block structures is a challenge to preparative chemistry. In a series of proceeding papers we have tried to contribute to this problem by syntheses of thermoreversible elastomers, which contain cellulose derivatives as the outer hardblocks (1) - (7). In the following a synthesis strategy for guayule rubber centered threeblock copolymers is discussed (8) (9).

Effective phase segregation of the blocks is the pre-condition for thermoreversible crosslinking and high mechanical niveau, consequently, of threeblock copolymers. The formation of block copolymers by combination of higher molecular weight prepolymers seems to be quite unrealistic because of incompatibility of the components. Preparation of guayule blocks with two endgroups capable to start polymerization of hardblocks is a much more promising approach to realize guayule rubber centered threeblock copolymers.

Because of its complexity we decided to attack the problem by an indirect approach, by testing the procedures with butyl rubber first. As a copolymer of isobutylene with a low percentage of isoprene butyl rubber appears to be the ideal model substance: Scission of double bonds by oxidation yields strictly difunctional telechelics. The block length of the telechelics is determined by the sequence length distribution within the macromolecular chains, which is known by copolymerization kinetics. The system allows conclusions being relevant for the corresponding studies on guayule.

RESULTS AND DISCUSSION

In the literature no effective way has been described up to our knowledge to realize strictly bifunctional cis-1,4-poly(isoprene) telechelics with adjustable block lenghts. Uncatalyzed as well as catalyzed scission of double bonds by oxygen, ozonolysis, decomposition with potassium permanganate and with nitrobenzene or with p-chlorophenylsyndones are discussed in this context. Scission of the double bonds by metathesis offers another chance for cis-1,4-poly(isoprene).

When studying critically the literature the best approaches for selective cleavage and functionalization of cis-1,4-poly(isoprene) may be direct partial scission of double bonds with RuO_4 or their partial epoxidation with subsequent scission of the epoxides by periodic acid .

Model studies with butyl rubber

Industrial butyl rubbers have been applied: Polysar^R 301 (P) with 1.52 mol-%, Total^R N 27 (T) with 1.59 mol-% and Esso^R 268 (E) with 1.66 mol-% isoprene.

GUIZARD and CHERADAME (10) have reported butyl rubber decomposition by RuO_4, with aliphatic peracids as co-oxidation catalysts. The peracids turned out, however, not to be the appropriate co-oxidation compounds because they may epoxidize the double bonds also, thus interfering the selectivity of the decomposition. H_5JO_6 or $NaJO_4$, respectively, showed up to be an appropriate co-oxidation agens. Cleavage with RuO_4 has been carried out heterogeneously in $CHCl_3$ or CCl_4, resp. Complete reaction has been reached, however, in the presence of phase transfer catalysts only. RuO_2 has been applied in catalytic amounts. $NaJO_4$ turned out to be the better co-oxidation agens when compared with H_5JO_6, because of faster RuO_2 oxidation to RuO_4.

RuO_2 cleavages have been carried out with butyl rubbers P and T. The agreement between calculated number average molecular weights - M_{nc} - and those determined for the telechelics by osmotic pressure - M_{no} - is excellent: $M_{ncP} = 3730$, $M_{noP} = 3750$, and $M_{ncT} = 3570$, $M_{noT} = 3670$.

According to DREYFUSS and KENNEDY (11) the epoxidation of butyl rubber runs very fast and selective. Consequently, epoxidation has been carried out at butyl rubbers P, T and E with m-chlorobenzoic acid, at 0° C in order to avoid degradation of the butyl rubber. Scission of the epoxide groups has been performed with periodic acid in THF. The telechelic poly(isobutylene) oligomers as obtained by both the RuO_4 and the epoxidation method are converted to α,ω- poly(isobutylene) diols via $LiAlH_4$. Combining osmotic M_n with those determined by OH-end-group analysis they turned out to be difunctional within ± 3 %.

The α,ω - poly(isobutylene) diols may be converted to bifunctional macroinitiators in a parallel manner as discussed below for the corresponding cis-1,4-poly(isoprene) telechelics in order to form poly(isobutylene) centered block copolymers.

Difunctional cis-1,4-poly(isoprene) macroinitiators

The $RuO_2/NaJO_4$ method turned out to be not applicable for cis-1,4-poly(isoprene). It did not succeed to control the heterogeneous cleavage reaction satisfactory. More satisfying conditions are realizable when cleaving in homogeneous CCl_4 solution, with RuO_4 - at higher concentration - as the sole oxidation agens. Then the subsequent removal of the RuO_2 caused difficulties, however.

Partial epoxidation of cis-1,4-poly(isoprene) has been acheived without difficulties. It turned out, however, that an additional decomposition of the PIP-chains occured by the periodic acid action: The M_n of the received blocks is lower than predicted from the degree of epoxidation, for all types of cis-1,4-poly(isoprene), natural and guayule as well as synthetic rubber. Analysis demonstrates that some epoxide groups are present only in natural rubber prior to reaction.

Therefore we studied the direct cleavage of cis-1,4-poly(isoprene) by H_5JO_6. At room temperature it runs only slowly and with low conversion. Just because of that it seemed to be applicable to the purpose to yield telechelics. The double logarithmic plot conversion and M_n, resp., versus reaction time (Figure 1) demonstrates that the cleavage does not follow strictly first order kinetics. The cleavage slows down significantly after a faster scission period. The relationship may be applied to realize telechelics of desirable average degree of polymerization, with one aldehyde and one keto endgroup.

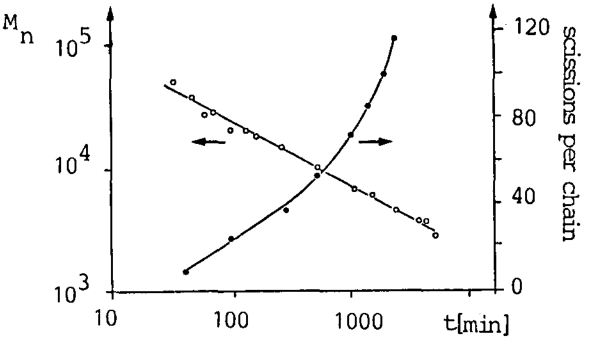

Figure 1: w.-% scissed double bonds and M_n, resp., vs. reaction time for guayule rubber, 0.44 mol / l, in toluene-ethanol (6 : 1 by vol.), at 22° C

It is interesting to note that the rate of scission increases with the number of methyl substituents at the macromolecular backbone, as verified by parallel measurements on 1,4-poly(butadiene)s and on trans-1,4-poly(isoprene) (guttapercha). The influence of configuration is a minor one.

The selectivity of the decomposition has been tested before and after conversion to α-ω-diols by determining the dependence of M_n on consumed oxidation agens, by N_2 and by UV analysis of the derivatives with dinitrophenylhydrazide, by OH analysis of the α-ω-diols and by testing the decomposition products with respect to unscissed 1,2-diols. The osmotic number average molecular weights of the telechelics received by periodic acid cleavage agreed with those calculated from H_5JO_6 consumption within ± 3 %, with those from N_2 content within ± 5 % and with those from UV analysis within ± 3 %. The bifunctionality is assured, consequently, within ± 0.07. For the α-ω-diols the osmotic M_n have been compared with chemical OH analysis and with OH determination of the 4-toluenesulfonylisocyanate derivatives by ^{1}H-NMR. A functionality around 2.05 ± 5 % has been found with both the methods. Finally it has been proved that unscissed 1,2-diols are not present. When adding lead tetraacetate no further decomposition of guayule oligomers has been observed.

Bifunctional macroinitiators have been obtained by addition of trityl potassium in THF solution, under air and moisture exclusion,

- from the telechelics with aldehyde and keto endgroups, resp., yielding potassium enolate terminated telechelics
- and from the α-ω-diols received via $LiAlH_4$, yielding potassium alcoholates.

The selectivity of the trityl potassium metallation has been checked by titrating a THF solution of non-cleaved cis-1,4-poly(isoprene) with trityl potassium solution. The red color appearing with the first drop stands more than half an hour. The agens does not react with the double bonds of the polymer.

Anionic polymerization of threeblock copolymers via macroinitiator

Because of their relatively low basicity K-enolates as well as K-alcoholates are able to induce polymerization of monomers with strong electron acceptor groups only. Methylmethacrylate seemed to be the most appropriate monomer to build up hardblocks with practicable glass transition temperature and with good phase separation against cis-1,4-poly(isoprene).

Polymerization is carried out in in THF at 25° C under exclusion of air and moisture. Adding MMA the viscosity of the medium is lowered through break-down of the association of the macroinitiator molecules. Around half of the MMA builds up hard blocks, the other half is homopolymerizing with both the macroinitiator systems. Transfer of the anions due to metallization and alcoholysis, resp., may cause the major effect. The dialcoholate turned out to be favourable to the dienolate system with respect to homopolymer cis-1,4-poly(isoprene) content, around 3 % with dialcoholate and around 10 % with the dienolate macroinitiator. Elastic homopolymer is deteriorating drastically the mechanical properties of a threeblockcopolymer, whereas a high glassy homopolymer content contributes to the thermoreversible crosslink domaines. Threeblock copolymers via K-alcoholate could be applied for applicational studies directly. We preferred, however, to isolate the threeblocks by extraction procedures prior testing.

Fivefold extraction with ethanol / acetone / Water (4 : 4 : 1) yields PMMA in the filtrate, fivefold extraction of the unsoluble part with petrol ether removed the homopolymer PIP, together with some blockcopolymer with high PIP content. The effectivity of the extraction procedures has been verified by GPC runs.

Analysis of the threeblock copolymers has been carried out by ^{1}H-NMR. The length of the middle block has been obtained by comparing the M_n of the products before and after decomposing the PIP block. It turned out that the blockcopolymers initiated with α,ω-cis-1,4-poly(isoprene) - K-alcoholate contain 1.93 PMMA blocks per PIP block, the - dienolate initiated 1.80, respectively.

Attempts to apply 4- and 2- vinylpyridine for block polymerization yielded oligomerization only. With methacrylonitrile crosslinked systems have been obtained.

Mechanical properties of poly(methylmethacrylate) - (b - cis-1,4-poly-(isoprene)) threeblock copolymers

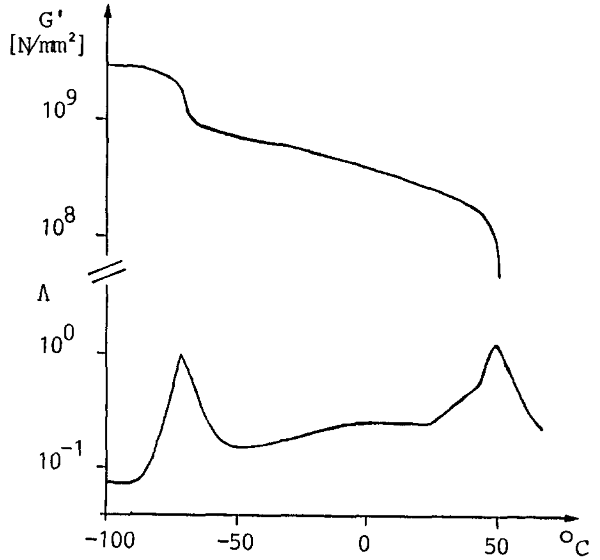

Figure 2: G' and G'' versus temperature of the threeblock copolymer described in the text. Torsion pendulum LONZA, ∿1 Hz, elongation at 50° C = 30 %

Figure 2 presents storage and loss modulus of a threeblock copolymer synthesized using a K-dialcoholate macroinitiator. The sample exhibits a M_n = 42100 and a cis-1,4-poly(isoprene) (Guayule) content of 59.0 %. It contains 1.93 PMMA blocks per PIP block. Between the two glass transitions of PIS and PMMA a rubberelastic plateau is observed. The decrease of G' with temperature indicates moderate phase separation of the domains. It may be noted that T_g of the hard blocks is lowered around 50° when compared with homopolymer PMMA. Apparently significant intermixing of the components causes a well developed interphase.

Elasticity moduli at 300 % elongation range from 10 to 30 kg cm^{-2}, elongations at break from 380 to 550 %, depending on M_n and ratio of the components. Significant indication for stress induced crystallization are observed only for samples with longer glassy blocks. The niveau of elongations at break is comparable to that of poly(styrene)-(b-poly(butadiene)) threeblock copolymers.

EXPERIMENTAL

Butyl rubber telechelics

Degradation with RuO_2 and $NaJO_4$

The 2 % solution of butyl rubber in cyclohexane is filtered and precititated in acetone. The polymer is dried in vacuo.

In a 1 l Erlenmeyer flask 200 ml 5 % aqueous $NAJO_4$ solution is dropped into 30 mg Ruthenium-IV-oxihydrate, 250 mg tricaprylyle methylammoniumchloride as phase transfer catalyst and 250 ml carbon tetrachloride. The mixture is stirred until the black RuO_2 is converted to the light yellow RuO_4. 500 ml of the butyl rubber solution is added slowly, with subsequent stirring until the RuO_4 colour appears.

After separation the CCl_4 phase is washed four times with aqua dest. and stirred subsequently with 100 ml of a 10 % aqueous KJ solution and with a diluted HCl solution. After treatment the p_H of the aqueous phase should range between 3 and 4. Having removed the aqueous phase the CCl_4 solution is washed three times with water. The generated iodine is removed with an aqueous $Na_2S_2O_3$ solution. After having washed the CCl_4 phase two times more it is dried with $MgSO_4$. The CCl_4 is evaporated in a rotational voporizer, and the products are dried at 50° C in vacuo.

Epoxidation and cleavage with H_5JO_6

A solution of 3 g m-chloroperbenzoic acid in 50 ml chloroform is added at 0° C to a chloroform solution of 10 g purified butyl rubber. After 5 h reaction under ice water cooling the solution is precipitated with cold methanol. The epoxidized BR is solved in cyclohexane and washed four times with aqueous $NaHCO_3$ solution and with aqua dest. After twofold reprecipitation it is dried in vacuo.

After having solved 10 g of the epoxidized BR in 100 ml THF in a N_2 stream 100 ml of an aqueous 4 % H_5JO_6 solution in THF is added. The mixture is heated in the dark at 50° C for 5 h. Precipitated HJO_3 is removed by filtration. After evaporation of the THF in the filtrate the residue is extracted with chloroform, washed four times and treated like described in the foregoing.

$LiAlH_4$ reduction of carbonyl endgroups

50 ml absolute ethylether are dropped to 1 g $LiAlH_4$ in a N_2 stream with ice drying. A solution of 10 g of the telechelic in absolute ether is dropped with ice cooling into the $LiAlH_4$ dispersion. After boiling 4 h under reflux the excess $LiAlH_4$ is converted under ice cooling with 10 ml ethylacetate. After having added slowly 25 ml acetic acid the mixture is refluxed again for 30 min.

The etheric phase is washed three times with water. To remove acetic acid it is treated with 5 % aqueous $NaHCO_3$ solution. Being washed four times with water and being dried with $MgSO_4$ the ether is evaporized. The α-ω-poly(isobutylene) diols are dried in vacuo.

Difunctional cis-1,4-poly(isoprene) macroinitiators

Purification of guayule rubber

A 2.5 % solution in toluene is centrifuged for one hour at 10000 r. p. m. and decanted subsequently from impurities. The procedure is repeated four times. 1 l of the solution is poured into a solution of 12.5 g NaOH in 300 ml water and 200 ml ethanol. The mixture is stirred and heated then under nitrogen at 60° C for 4 h. The emulsion is stirred over night at room temperature. Subsequently it is washed with water five times, neutralized with CH_3COOH and washed again four times. The guayule rubber is precipitated in acetone and is extracted with acetone in a water cooled Soxhlet for 24 h. Then it is dried in vacuo.

Direct cleavage with H_5JO_6

15 g of purified guayule are solved under N_2 in 400 ml toluene. A solution of 7.5 g H_5JO_6 in ethanol / toluene (2 : 1) is added dropwise. The cleavage is stopped by adding water. The M_n of the telechelics is determined by the reaction time.

To remove HJO_3 the mixture is filtered. The filtrate is diluted with 400 ml petrolether and washed with water five times. After treating twice with 1 l 0.25 % aqueous Na_2SO_3 the solution of the telechelics is dried with $MgSO_4$. Then the solvent is removed with a rotary evaporator.

Conversion to macroinitiators

Conversion to K-dialcoholates starts with the α-ω-diols, which are received via $LiAlH_4$ as described for butyl rubber. The conversion of the telechelics to potassium dialcoholates and dienolates of cis-1,4-poly(isoprene) is performed on the vacuum line. The solution of 2.5 g telechelic in absolute benzene is freeze dried 5 h under high vacuum. 150 ml absolute THF are added, and titration with trityl potassium sulution is carried out up to the point where the red colour of the agens stands longer than 10 min.

Subsequently, by adding the appropriate amount of absolutized momomer, the block polymerisation is performed.

CONCLUSION

It has been demonstrated that syntheses of thermoreversibly crosslinked threeblock copolymers can be performed with guayule rubber as the elastic central block. Guayule based macroinitiators have been obtained by direct cleavage with periodic acid and subsequent conversion of the telechelics to diols and to K-dialcoholates, finally. Poly(methylmethacrylate) - (b-cis-1,4-poly(isoprene) threeblock copolymers with considerable niveau of properties have been obtained. It may be worthwile to optimize the polymerization process, with methylmethacrylate and with other monomers which exhibit strong electron acceptor groups.

In a parallel way poly(isobutylene) centered threeblock copolymers may be build up, with butyl rubber as the base of macroinitiator synthesis.

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REFERENCES

1. C. Feger and H.-J. Cantow, Polymer Bulletin **3**, 407 (1980)
2. C. Feger and H.-J. Cantow, Polymer Bulletin **6**, 321 (1982)
3. C. Feger and H.-J. Cantow, Polymer Bulletin **6**, 583 (1982)
4. Th. Mezger and H.-J. Cantow, Angew. Makromol. Chem. **116**, 13 (1983)
5. Th. Mezger and H.-J. Cantow, Makromol. Chem. Rapid Commun. **4**, 313 (1983)
6. Th. Mezger and H.-J. Cantow, Polymer Bulletin **9**, 515 (1983)
7. H.-J. Cantow, C. Feger, T. Mezger and J. Solache, Makromol. Chem., in press
8. H.-J. Cantow, Th. Mezger, J. Solache and M. Khan, Proc. IUPAC MAKRO Amherst 164 (1982)
9. J. Solache Orozco, Dissertation Freiburg i. Br. (1984)
10. C. Guizard and H. Cheradame, Europ. Pol. J. **17**, 121 (1981)
11. P. Dreyfuss and J. Kennedy, Analyt. Chem. **47**, 771 (1975)

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