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Cellulose Containing Block Copolymers

1. Synthesis of Trimethylcellulose-(b-Poly(Oxytetramethylene))– Star Block Copolymers

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SUMMARY

The preparation steps leading to trimethylcellulose - (b-poly(oxytetramethylene)) - block copolymers of the star type are described. This includes the synthesis of fully substituted cellulose derivative blocks each with one reactive endgroup by partial cleavage of trimethylcellulose, the activation of those endgroups to initiate the living cationic polymerization of poly(oxytetramethylene) - blocks and coupling of the resulting two-blocks by poly(4 - vinylpyridine) to form starshaped block copolymers.

INTRODUCTION

The oil crisis has turned scientific as well as industrial activities towards the chemical use of regrowing raw materials. The most important natural feed stock is cellulose with an annual production around 100 billion metric tons. Because of its macromolecular backbone, cellulose is of interest not only for conversion into low molecular weight compounds, but it is suitable for the synthesis of polymeric derivatives also.

Already in the beginning of industrial polymer manufacturing many cellulose based polymers have been prepared. Thermoplastics like cellulose acetobutyrate are still of technical interest. Other interesting cellulose derivatives have been synthesized by graft polymerization techniques. Cellulose containing block copolymers should offer a broad variety of useful properties, especially within the region of thermoplastic processable elastomers.

First steps to realize such cellulose containing thermoreversible elastomers were done by synthesis of segmented copolymers built up by polyethers and -esters, respectively, diisocyanates and oligomer cellulose derivatives containing hydroxyl end groups [1-3]. Films and fibers produced in such ways, however, showed up relatively poor mechanical properties because of the unsufficient length of the hard blocks. In consequence phase separation is poor. More satisfying segregation

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of the phases and improved mechanical properties consequently should be expected for block copolymers exhibiting longer blocks. In the following a method is described to synthesize cellulose containing block copolymers with block molecular weights of more than 10 000 dalton.

SYNTHESIS STRATEGY

The formation of block copolymers by combination of high molecular weight prepolymers seems to be quite unrealistic because of incompatibility of the chemically different blocks, with the exception of reactions between living macroanions and -cations. A more promising concept seems to be the polymerization of the one component onto the active end of a preformed macromolecular block. Coupling of the resulting twoblocks leads to threeblock copolymers, if difunctional couplers are used. By this method a certain amount of uncoupled twoblocks can not be avoided. Such twoblocks, however, significantly lower the niveau of the mechanical properties. Coupling with multifunctional systems yields starshaped block copolymers with negligible amounts of twoblocks and is therefore preferable. Furthermore, star block copolymers exhibit better processibility when compared with linear macromolecules of identical molecular weight. It has been shown that the zero gradient melt viscosity primilarily depends on the "span length" of the star, not on its functionality 4).

Thus the following strategy has been developed for the synthesis of starshaped cellulose containing·block copolymers:

1. Synthesis of fully substituted cellulose derivatives
2. Partial degradation of the cellulose derivatives to produce fully substituted cellulose blocks which contain one reactive endgroup each
3. Activation of these endgroups to initiate the polymerization of the second block
4. Polymerization yielding twoblock copolymers
5. Coupling of these blocks by multifunctional reagents to realize starshaped block copolymers.

Two types of polyreactions turned out to be appropriate to form the soft blocks, namely living cationic and free radical mechanisms. In this paper only the polymerization of tetrahydrofurane[THF] by living cationic mechanism is concerned.

TRIMETHYLCELLULOSE BLOCKS

The living cationic block copolymerization of THF requires a cellulose derivative block, which does not undergo termination or transfer reactions with the reactive oxoniumion of the growing poly(tetramethylene)[POTM]-chain.

Trimethylcellulose [TMC] fulfills these requirements, as was shown by the polymerization of THF in the presence of TMC homopolymer. TMC, however, is not processable thermoplastically, because its melting range is above 300° C, near its decomposition. Thermoplasticity, however, can be reached in mixed substituted cellulose ethers. Nevertheless for the basic investigation the trimethyl cellulose was chosen, because its structure is comparably uncomplicated. Thus investigations on the mechanical properties are not affected in a complex way by a chemical heterogeneity of the cellulosic blocks.

To get TMC - blocks with one reactive endgroup a hig molecular TMC was cleaved partially by 1 n hydrogene chloride at 30° C in a 4/1 methylene chloride - benzene mixture. The kinetics of this reaction are expressed by 5)

$$\ln(1-1/P_o) - \ln(1-1/P_t) = k_1 t \quad . \qquad (1)$$

P_o and P_t, resp., mean the number average degrees of polymerization at times t=0 and =t; k_1 is the rate constant.

The cleavage scheme is given in Figure 1. Figure 2 shows a rate constant $k_1 = 1.912 \cdot 10^{-4}$ min^{-1} at 30° C.

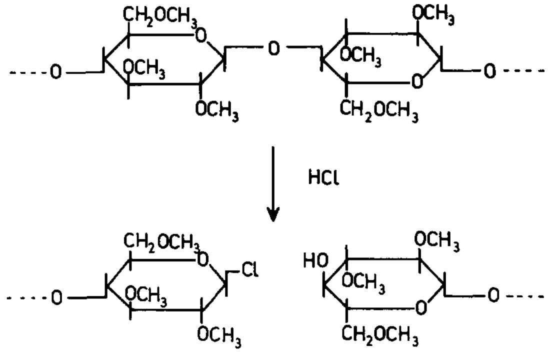


Figure 1: Cleavage of trimethyl cellulose with hydrogene chloride in an aprotic medium

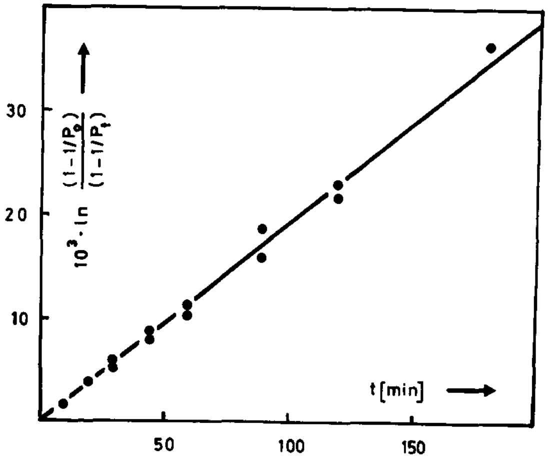
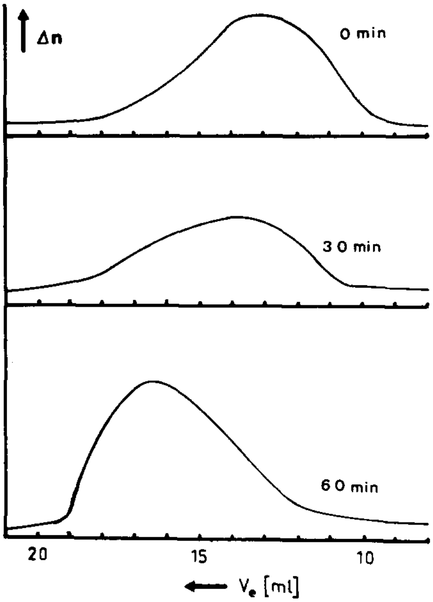


Figure 2: Kinetics of the cleavage reaction of TMC (M_n = 120000), 20 mg ml^{-1} in 4/1 CH_2Cl_2- benzene by 1 n dry HCl at 30° C (see Equ. 1)



TMC - block lengths may be adjusted quantitatively on this base. The endstanding glucosidylchlorides formed at the blocks offer the base for subsequent polymerization of the second block onto the one end. The molecular weight distribution of the TMC - block turns out to be rather broad and - at low conversions - similar to that of the educt $^{6)}$. This is demonstrated by the GPC elution curves of samples analyzed after different cleavage times (Figure 3).

Figure 3: Gel permeation chromatography elution curves of trimethylcellulose blocks produced by cleavage with dry HCl in aprotic media after various reaction times. V_e = elution valume, Δn = refractive index difference.

BLOCK COPOLYMERIZATION OF TETRAHYDROFURANE

The TMC - blocks containing one α - chloro ether end were treated with silver hexafluoroantimonate, $AgSbF_6$, in THF solution between -10^{o} and $+23^{o}$ C. Thus a carbocation is formed which initiates a living cationic THF polymerization (Figure 4). The living type character of the polyreaction was confirmed by polymerizing THF in the presence of unactivated TMC. Partial termination occured during this reaction due to impurities in the macromolecular TMC, but not by transfer reactions. If the latter would occur, TMC(g - POTM) - graft copolymer as well as POTM-homopolymer should be formed according to Figure 5. Graft copolymers, however, could not be detected by very sensitive solubility analyses $^{7)}$.

After low conversion the THF polymerization is terminated either by methanolic KOH producing TMC - POTM - twoblock copolymers or by low molecular weight poly(4 - vinylpyridine) $P_n \sim 20$) yielding TMC - POTM - starshaped block copolymers (Figure 6). Star blocks, however, are preferable from an applicational standpoint not only because of their better processability. They exhibit more pronounced phase separation also even at lower block lengths$^{8)}$.

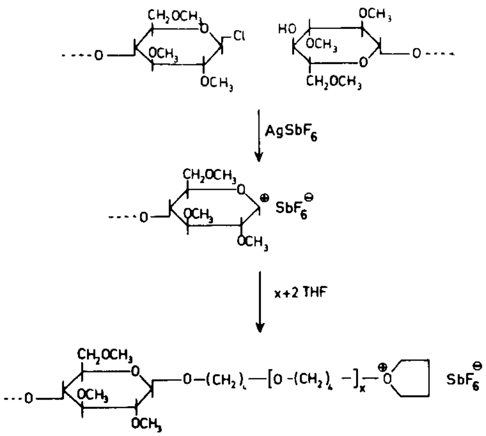


Figure 4: Synthesis of TMC-POTM twoblock copolymers starting with an α- chloro ether end of the TMC

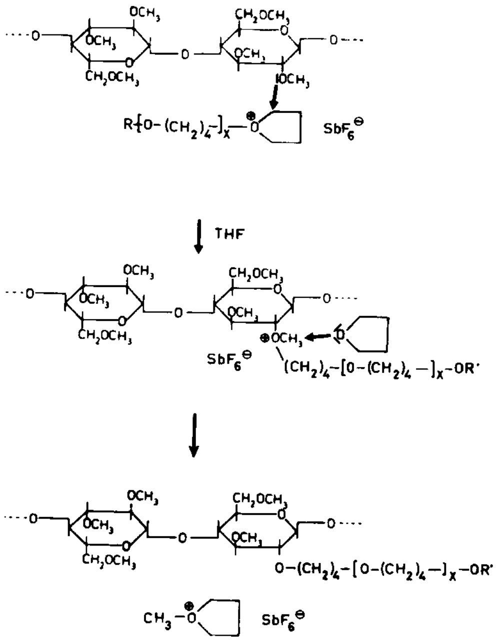


Figure 5: Scheme of TMC (g-POTM) graft copolymerization

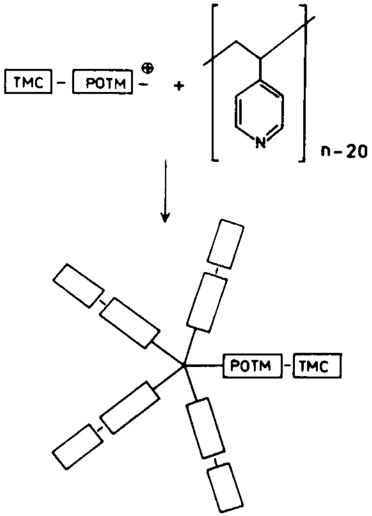


Figure 6: Formation of star blocks by coupling of living cation ended TMC- POTM twoblock copolymers by low molecular poly(4- vinylpyridine)

EXPERIMENTAL

TRIMETHYLCELLULOSE

TMC was synthesized starting from Tylose® MH 4000 (Kalle AG) according to KEILICH et al. 9). First it was characterized concerning its hydroxyl group content by reaction with trichloroacetyl isocyanate in refluxing CH_2Cl_2 with diaza - [2.2.2] - bicyclooctane as catalyst and by subsequent elementary analysis. A hydroxyl group content near zero was found in this way. Second the molecular weight was determined by the STAUDINGER index [η] in l g^{-1} according to the relationship established with osmometry10) in $CHCl_3$ at 30° C :

$$[\eta] = 2.171 \cdot 10^{-5} M_n^{0.86}$$

M_n of the educt turned out to be about 120 000 dalton typically.

ACIDOLYTIC DEGRADATION

2 g TMC are solved in 80 ml CH_2Cl_2 and 20 ml benzene. The solution was dried over P_2O_5.A saturated solution of HCl in diethylether is added at 30° C up to 1 normality. When the desired TMC block length is reached - after 30 min typically - the sample is cooled down to - 50° C, and the solvent is evaporated. The benzene content induces freeze drying at the end of the evaporation.

BLOCK COPOLYMERIZATION

2 g TMC are solved in 150 ml purissimum THF. $AgSbF_6$ (Ventron product without further purification) was added to the thermoconstant solution (10° C) in small excess.
Near immediately an AgCl precipitation is observed. After having formed a POTM block of the desired length (2 h for instance), the reaction either is terminated by adding methanolic KOH (1 g l^{-1}) containing a small amount of KCN (0.2 g l^{-1}) or by adding 2.5 ml solution of anionically produced 11) low molecular weight poly(4- vinylpyridine) in CH_2Cl_2 (15 mg ml^{-1}) being purified over a sodium mirror. After stirring for about 30 min the star shaped block copolymer formed by the latter procedure is precipitated in petrol ether (40- 65° C) and dried under vacuum. The yield is depending on polymerization time.

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REFERENCES

1. STEINMANN, H. W., Polym. Prepr. 11(1), 285 (1970)
2. KIM, S., STANNETT, V. T. and GILBERT, R. D. J. Polym. Sci., Pol. Lett. Ed. 11, 731 (1973)
3. POHJOLA, L. HARVA, O. and KARVINEN, J. Finn. Chem. Lett. 221 (1974)
4. BAUER, B. J. and FETTERS, L. J. Rubber Revs. 51, 406 (1978)
5. Mc BURNEY, L. F., Degradation of Cellulose, in Cellulose, Edts.: OTT , E., SPURLIN, H. M. and GRAFFLIN, M. W. High Polymers Vol. V, Part I, Interscience New York, p. 99 (1954)
6. HUSEMANN, E. and SCHULZ, G. V., Z. physik. Chem. B52, 1 (1942)
7. MOLAU, G. E., Colloidal and Morphological Behaviour of Block and Graft Copolymers, Edt.: AGGARWAL, S. L., Plenum Press, pp. 79- 106 (1970)
8. MANTIEL, R., KUO, C. and Mc INTIRE, D. Polym. Prepr. 15(2), 169 (1974)
9. KEILICH, G., SALMINEN, S. and HUSEMANN, E. Makromol. Chem. 141, 117 (1971)
10. FEGER, C., Thesis Freiburg i. Br. (1980)
11. SPIEGELMAN, P. P. and PARRAVANO, G. J. Polym. Sci. A2, 2245 (1964)

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