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Telechelics

Functionalization of Soluble Polymers

6. Preparation and Kinetic Aspects of Linear, Hydrophilic Aldehydes Based on Poly(Oxyethylene)

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SUMMARY

The synthesis of di-(4-formylphenyloxyethyl) poly(oxyethylene) and the corresponding oxime derivative are described. Kinetic aspects of the reaction of the dichloro telechelic with 4-hydroxy benzaldehyde are investigated and discussed.

INTRODUCTION

Soluble polymers with a linear and hydrophilic chain have been investigated in terms of their application as telechelics (MUTTER 1978, GECKELER 1979, BAYER et al. 1982, ANZINGER and MUTTER 1982). A number of functional groups have been studied but investigations on aldehyde telechelics have not been reported so far. Syntheses of soluble and cross-linked polymers with aldehyde groups based on polystyrene have been described (GIBSON 1975, GIBSON and BAILEY 1976, GECKELER et al. 1983). However, there are essential differences in properties and applications between linear telechelics and multifunctional polymers. Therefore, a procedure for easy preparation of aldehyde telechelics and the kinetic aspects of this formation reaction are described in this paper.

RESULTS AND DISCUSSION

The conversion of compound $\underline{1}$ to the polymer aldehyde $\underline{3}$ was investigated in dependence of time at different temperatures. It could be shown that maximum conversion was reached at a temperature of 130°C after 3 hours (Fig. 1). At 80°C, the reaction has not been completed even after 15 hours. A linear dependence of time was found for the reaction at 22°C but in this case only 20 % of conversion have been reached after 15 days.

$$\underset{\underline{1}}{P\text{-}CH_2\text{-}CH_2\text{-}Cl} \xrightarrow[\underline{2}]{NaO\text{-}C_6H_4\text{-}CHO} \underset{\underline{3}}{P\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C_6H_4\text{-}CHO}$$

$$\underline{3} \xrightarrow{NH_2OH} P\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C_6H_4\text{-}CH{=}NOH \quad \underline{4}$$

P = Poly(oxyethylene) chain containing the identical functional group

From these findings practical consequences for functionalization reactions of hydrophilic telechelics can be drawn. For usual applications of polymer-analogous reactions quantitative conversion is optimum and therefore reaction temperatures below 100°C are not recommendable. Otherwise complete conversion cannot be guaranteed within 24 hours. On the other hand, the soluble polymers should be allowed to react at temperatures between 20 and 80°C if only partial functionalization is desirable. Thus, the degree of functionalization can be easily altered by variation of the reaction time.

The stability of the poly(oxyethylene) chain during the functionalization reactions was checked by gelpermeation chromatography. After two polymer-analogous reactions there was no significant change of the molecular mass distribution of the polymers. In order to verify the existence of the aldehyde functions in the polymer, besides the data from analytical and spectroscopical investigations, the chemical availability was proved by derivatization with hydroxylamine. Finally, the oxime derivative of the polymer (4) has been proved by IR and ^{13}C-NMR spectroscopy.

EXPERIMENTAL

All chemicals were purified and dried as described in previous papers of the series.

Di(4-formylphenyloxyethyl)poly(oxyethylene) (3) :

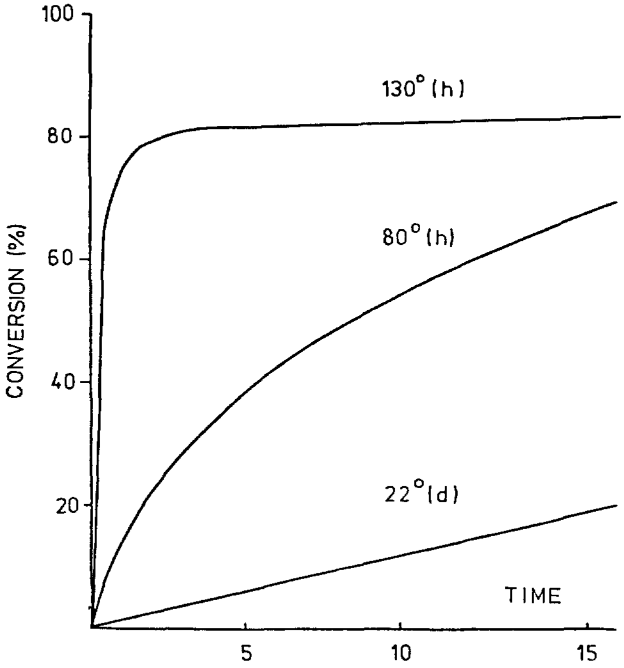
To a solution of 12.32 g (8 mmol) of dichloro poly(oxyethylene) ($\overline{M}$ = 1500) in 100 ml dimethylformamide, 2.88 g (20 mmol) of 4-hydroxybenzaldehyde sodium salt was added under nitrogen. The clear solution was heated to 130°C for 24 h under reflux. It became turbid after half an hour indicating sodium chloride formation. After cooling, the mixture was filtered and then 1 l of diethylether was added slowly under stirring. After storage overnight in the refrigerator, the precipitated polymer was filtered off and washed with ether. The solid was dissolved in 200 ml of dichlormethane and 1 ml of 6 N hydrochloric acid was dropped to the solution under stirring. After 5 minutes 20 g of sodium sulfate and 2 g of activated carbon were added separately and the mixture was stirred for 2 hours. Then, the solution was filtered and the residue washed with 50 ml of dichlormethane. After reducing the volume of solution to about 100 ml, the polymer was precipitated twice by ether for purification and dried in vacuo at room temperature.

Yield: 12.8 g (92 %)
Fp. 37-39°C
DF: 0.96 (UV-spectroscopy)

Elemental analysis:			
	Calcd	C 57.19	H 8.52
	Found	C 56.58	H 9.03

Fig. 1.

Conversion as function of time and temperature for the reaction of dichloro poly(oxyethylene) (1) with 4-hydroxybenzaldehyde (2). Determination was carried out by UV-spectroscopy at 274 nm. The units of the abscissa are referred to hours for 130°C and 80°C and to days for 22°C



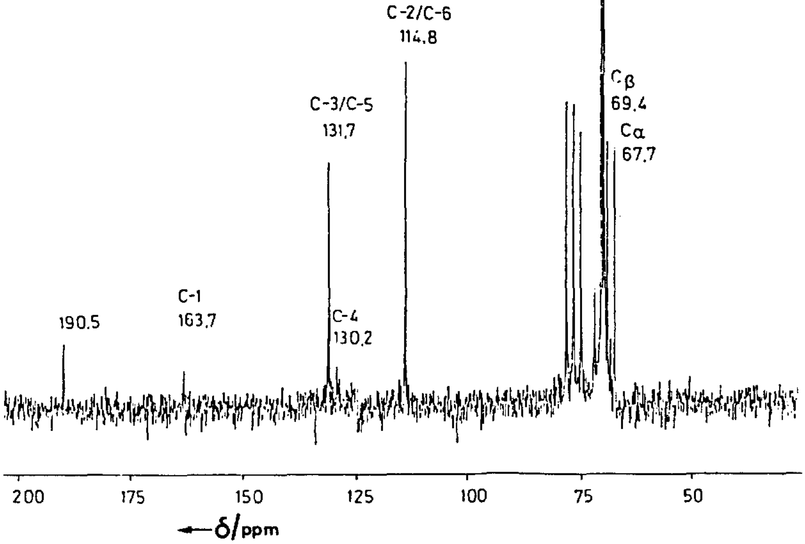


Fig. 2. ^{13}C-NMR spectrum of polymer 3 in $CDCl_3$ (20.115 MHz)

UV (EtOH): εmax (λ = 274 nm) = 3.14 10^4 l $cm^{-1}mol^{-1}$
IR(KBr): 1695 (m; CHO), 1600, 1506 (m; C_6H_4), 1460, 1350
(s; CH_2), 1100 (vs; COC) cm^{-1}
^{13}C-NMR ($CDCl_3$): δ = 190.5 (-CHO) (Fig. 2)

Kinetic investigation of the formation of polymer (3):

4.0 g of dichloro poly(oxyethylene) (1) (5.2 mmol Cl) was dissolved in 40 ml dimethylformamide at the defined temperature (22°, 80°, 130°C). To this solution, 0.64 g (5.2 mm of 4-hydroxybenzaldehyde sodium salt (2) was added rapidly and the solution was kept at the defined temperature under stirring. Samples were taken after 0.5, 1, 2, 3, 4, 6, 9, 12, 24 hours or days respectively. To this end, 3 ml of the reaction solution was dropped into 40 ml diethylether under ice-cooling, the precipitated polymer was filtered off and dissolved in 20 ml dichloromethane. After addition of two drops of 6 N hydrochloric acid and 4 g of sodium sulfate, the mixture was shaken and allowed to stand for two hours. Then, the solution was filtered and the volume reduced to 3 ml in vacuo. After precipitation by ether the sample was washed, dried over P_2O_5 in vacuo and used for UV-spectroscopic determination.

Di(benzaldehyde oxime oxyethyl) poly(oxyethylene) (4):

To a solution of 0.85 g (0.5 mmol) of polymer aldehyde 2 in 5 ml pyridine, 0.35 g of hydroxylamine hydrochloride was added and the solution was kept at 110°C for 5 hours. After cooling, it was poured into 60 ml diethylether under stirring and the mixture was stored in the refrigerator overnight. Then, the polymer was filtered off, dissolved in dichloromethane and treated with sodium sulfate and activated carbon. The mixture was filtered, concentrated in vacuo and reprecipitated by ether. The product 3 was obtained after filtration and drying over P_2O_5 in vacuo.

Yield: 0.62 g (73 %)
Elemental analysis: Calcd N 1.69
Found N 1.36
DF: 0.81 (N-analysis)
IR(KBr): New bands at 1640 (w; C=N) and 940 (s; N-O) cm^{-1}; band at 1695 (C=O) cm^{-1} disappeared.
^{13}C-NMR ($CDCl_3$): δ = 149.3 (-CH=N-).

REFERENCES

ANZINGER, H. and MUTTER, M.: Polym. Bull. 6, 595 (1982)
BAYER, E., ZHENG, H., and GECKELER, K.: Polym. Bull. 8, 585 (1982)
GECKELER, K.: Polym. Bull. 1, 427 (1979)
GECKELER, K., ZHENG, H., and BAYER, E.: J. Polym. Sci. 21, 3541 (1983)
GIBSON, H.W.: Macromol. 8, 89 (1975)
GIBSON, H.W., and BAILEY, F.C.: J. Polym. Sci. 14, 1661 (1976)
MUTTER, M.: Tetrahed. Lett. 31, 2843 (1978)

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