Polymer Bulletin 1, 199–204 (1978)

Polymer Bulletin

Degradation of Poly(ester)s by Carbenium Ions

Manfred L. Hallensleben and Knut Möller

Institut für makromolekulare Chemie der Universität, 7800 Freiburg,
Federal Republic of Germany

SYNOPSIS

Poly(ester)s are degraded by the attack of classical carbenium ions. In a representative study it is demonstrated that the carbenium ions are by far more reactive to cleave ester linkages than are protons. The change of molecular weight distribution of the poly(ester) during reaction with carbenium ions is reported In an example on low molecular weight compounds the reaction path has been clarified.

INTRODUCTION

Recently our laboratory has presented evidence that cationic polymerization of styrene monomer in the presence of poly(ester)s leads to copolymer formation via cationic chain transfer from the carbocation chain end of the growing vinyl polymer species to the ester linkage (HALLENSLEBEN et al. 1977a) (HALLENSLEBEN 1977b) (MÖLLER 1977) (FRITZ et al. 1978). Since no information on the cleavage of esters upon carbocation attack is available from the literature, on the other hand a precise knowledge of the nature of cation formed from the reaction is necessary to argue on a chain transfer mechanism in a polymerization reaction, we undertook an investigation on what happens to the molecular weight distribution of a given poly(ester) upon carbenium ion attack and on an appropriate model compound example the mechanism of ester cleavage.

We have been able to demonstrate that in styrene polymerization with cationic initiators and poly(p-xylylene succinate) acting as a chain transfer polymer up to 30% of converted styrene is incorporated in copolymers which were isolated by fractionation, and no poly(ester) remains unreacted (HALLENSLEBEN, MÖLLER 1978).

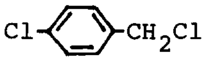
The present communication intends to shed more light on the mechanism involved in the chain transfer reaction of the poly(styrylium) cation to an ester linkage in a poly(ester).

EXPERIMENTAL

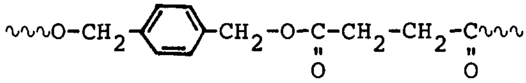
Benzylchloride <u>3</u>, p-chloro benzylchloride <u>1</u>, meth-

0170-0839/78/0001/0199/$01.20

ylen dichloride, and benzene were dried and operated as is well established for cationic polymerization. Silverperchlorate (MERCK) was azeotropically dried with toluene, silvertetrafluoroborate (FLUKA), deutero-nitromethane, and deutero-methylene dichloride (SHARP&DOHME) were used as supplied. Poly(ester) 2 was prepared by polycondensation reaction in toluene. For further experiments the high molecular weight tail after fractionation was used ($\bar{M}_{n\ osm}$ = 3290 g/mol, $[\eta]$= 0,0206 l/g) and no precautions were taken to protect HO- and HOOC-end groups. Ester 5 was characterized by proton-nmr.



1



2

For the degradation experiments first the cations were generated in solution from 1 with silvertetrafluoroborate; 5min later the poly(ester) solution and - so wanted - water were added, all concentrations are given in Tab.1 and 2, respectively. Degraded polymer was recovered by precipitation from the filtered reaction solution in excess methanol. $[\eta]$ values were determined with an OSTWALD viscometer at 293K. Osmotic molecular weights were determined with a PERKIN-ELMER instrument model 115 in chloroform. GPC traces were recorded in chloroform solution at 298K. The GPC traces were drawn by taking into account the amount of recovered polymer of the corresponding experiments.

As a model reaction for the ester cleavage of poly(p-xylylene succinate) 2 by the carbocation chain end of poly(styrylium) cations, benzylium cations 4 were generated with silverperchlorate and reacted with 2-phenylisopropyl acetate 5 in deutero-methylene dichloride, deutero-nitromethane, and benzene solutions, respectively. Experiments were carried out in .1M solutions at 293K under an atmosphere of pure nitrogen and magnetic stirring. After a reaction time of 15min some drops of water and a small amount of potassium carbonate were added, the solution was filtered through a sintered glass disk, and thoroughly concentrated for proton-nmr investigation. The number of reaction products was identified by GC from the reaction solution. The proton-nmr spectra were recorded with a 60 MHz JEOL JNM PMX60 spectrometer and TMS as internal standard.

RESULTS

Degradation of poly(ester) 2 by benzylium cations

To be sure that predominantly cations, and not protons are the poly(ester) degrading species, reactions were carried out under cationic polymerization con-

Table 1

Reaction of 6 with 2 in the Presence of Water

Exp. Nr.	$[2]^{a,b}$	$[6]^{a}$	$[H_2O]^{a}$	Recovered Polymer (g)	(%)^{c}	$[\eta]\cdot 10^2$ (l/g)^{d}
1	50	50	0	.35	31.8	.27
2	50	50	5	.28	25.5	.40
3	50	50	50	.46	41.8	1.02
4	50	50	500	.90	81.8	1.27
5	50	5	0	.86	78.2	1.42
6	50	5	5	.89	80.9	1.58
7	50	5	50	.93	84.5	1.83
8	50	.5	0	1.08	98.2	2.06
9	50	.5	5	1.09	99.1	2.06
10	50	.5	50	1.09	99.1	2.05

a) concentrations are given in mmol/l, b) [2] are given as mmol ester linkages/l, c) 1.1 g correspond to 100% recovering, d) determined in methylene dichloride solution at 293K

reaction temperature: 293K, reaction time: 18hrs., solvent: methylene dichloride, 6 generated by the reaction of 1 with silvertetrafluoroborate

Table 2

Time Dependence of 2 Degradation by 6 Cations

Exp. Nr.	$[2]^{a,b}$	$[6]^{a}$	Reaction Time (hrs.)	Recovered Polymer (g)	(%)^{c}	$[\eta]\cdot 10^2$ (l/g)^{d}
1	50	50	18	.35	31.8	.27
12	50	50	6	.28	25.5	.67
13	50	50	3	.26	23.6	.57
14	50	50	1.5	.31	28.2	.46
15	50	50	.75	.20	18.1	.56
5	50	5	18	.86	78.2	1.42
16	50	5	9	.98	89.1	1.55
17	50	5	6	1.04	94.5	1.96
18	50	5	3	1.10	100	1.94

a, b, c, d), and reaction conditions are the same as in Tab.1

ditions. In addition, p-chlorobenzylium cations 6 were used in the degradation experiments because benzylium cations 4 undergo self-alkylation to a considerable extent, as will be shown later in this communication. To study the influence of protons on the reactions, some experiments were carried out in the presence of well defined amounts of water. The results of representative experiments are listed in Tab.1.

In addition to that compilation, Fig.1 demonstrates these results as GPC traces after reaction at given and constant reaction time. Since carbenium ions, in general, readily react with water to form protons, the conclusion is that the carbenium ion attack on ester linkages is the favored reaction and therefore degradation by protons in dry systems ($[H_2O] < 10^{-3}$ mol/l) can be neglected.

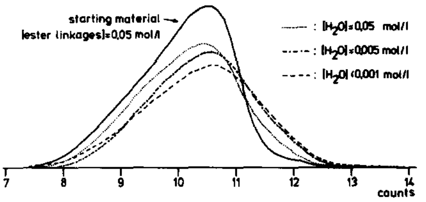


Fig.1: Influence of water on the degradation of 2 by 6 (experiments Nr. 5, 6, and 7 from Tab.1)

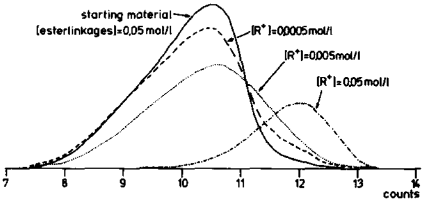


Fig.2: Degradation of 2 by 6 cations of different concentrations (experiments Nr. 1, 5, and 8 from Tab.1)

At low cation concentrations in the range of end group concentration, a little broadening of the molecular weight distribution is observed but no change in molecular weight, whereas at high cation concentrations only low molecular weight compounds are obtained already after .75 hrs. In case of an intermediate concentration, degradation causes a shift to lower molecular weight accompanied by a remarkable broadening of the distribution, see Fig.2.

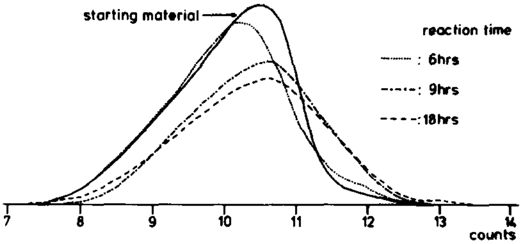
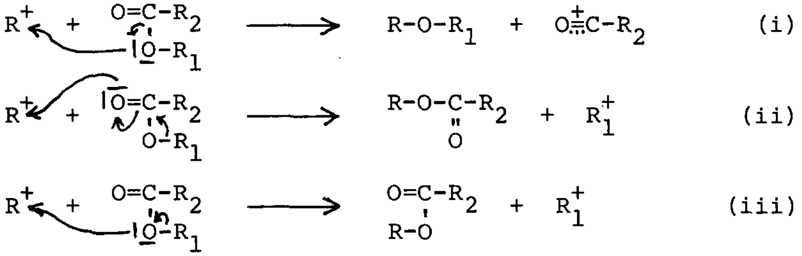


Fig.3: Time dependence of 2 degradation by 6 cations (experiments Nr. 5, 16, and 17 from Tab.2)

Looking on the change of molecular weight distribution under dry conditions over a long period of time in Fig.3 one observes that the unsymmetrical distribution curve of the starting material levels to a symmetrical one. This indicates a long living active species the chemical nature of which needs to be further investigated.

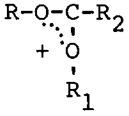
Mechanism of ester cleavage

In general, there are three possible ways by which a reaction between a carbenium ion and a carboxilic ester may proceed:



Whether reaction path (i) or either (ii) or (iii) is followed evidently will depend on the relative stability of the cations involved in the reaction.

A possible reaction intermediate is a dialkoxicarbenium ion 7 in path (ii):



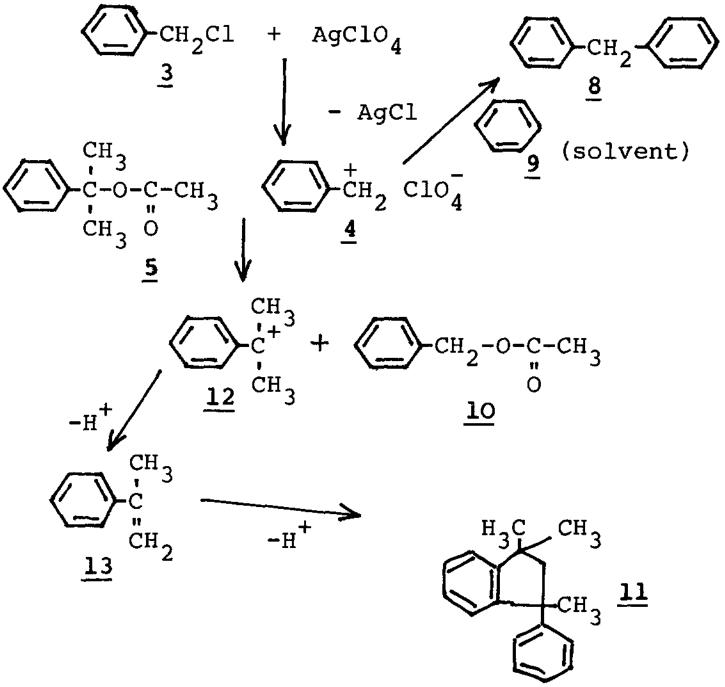
7

The reaction scheme which is followed including all solvents is given in scheme (iv). In benzene solution, the major reaction product is diphenyl methane 8 from the Friedel-Crafts reaction of the benzylium ion 4 with the solvent 9. However, a considerable amount of the ester 5 is cleaved by carbenium ion attack from which benzyl acetate 10 results. This reaction may proceed either along (ii) or (iii). 10 is accompanied by stoichiometric amounts of 1.1.3-trimethyl-3-phenyl indane 11 which was identified from proton-nmr of an authentic sample (BERGMANN et al. 1931).

However, in reaction scheme (iv) the equilibrium ester of 4 (PEPPER 1974) has to be considered.

ACKNOWLEDGEMENT

This work was supported by the Deutsche Forschungsgemeinschaft. Additional support by Fonds der Chemischen



Industrie and by Wissenschaftliche Gesellschaft in Freiburg is gratefully acknowledged.

REFERENCES

BERGMANN, E., TAUBADEL, H. and WEISS,H.: Chem. Ber. 64, 1493 (1931)

FRITZ, E., HALLENSLEBEN, M.L., HOSER, W.F., KUNZ, D., MASSEN, U., MÖLLER, K. and TSOLAKI, H.: Paper presented at the 1st European Discussion Meeting on New Developments in Ionic Polymerizations, Strasbourg, 27.2.-2.3.1978, Proceedings p. 57

HALLENSLEBEN, M.L., HOSER, W.F. and MÖLLER,K.: Paper presented at Makromolekulares Kolloquium, Freiburg, 3.-5.3.1977; see also Chemiker-Ztg. 101, 293 (1977)

HALLENSLEBEN, M.L.: Paper presented at MACRO DUBLIN, 17.-22.7.1977, Proceedings Vol. I, p. 89

HALLENSLEBEN, M.L. and MÖLLER, K.: Results 1978 to be published in this journal

MÖLLER, K.: Diploma thesis, University of Freiburg, 1977

PEPPER, D.C.: Makromol. Chem. 175, 1077 (1974); a comment on that by Prof.R.W.LENZ is acknowledged

Received October 5, 1978