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Direct monitoring of cationic polymerization by temperature, conductivity and permittivity measurements

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Summary

Direct monitoring of cationic polymerization was accomplished by simultaneous measurement of the average dielectric constant, representing the dipoles, of the conductivity, produced by unpaired ions, and of the temperature, characteristic for reaction rate. The ionogenic equilibria during the living polymerization of isobutylene by 1,3,5-tris(2-methoxy-2-propyl)benzene/BCl_3 in CH_2Cl_2 at -25°C were demonstrated. Temperature, resistance and capacitance were measured directly in the reaction mixture by a specially designed instrument.

Both the conductivity and the average dielectric constant change characteristically during the living polymerization, indicating the presence and simultaneous change of unpaired ions and strongly polarized species.

The differences between the AMI, and the aging technique were demonstrated and explained. In the latter case slow initiation was observed due to the methoxy-chlorine exchange caused by a reaction with BCl_3.

The applied direct monitoring method helps to understand the role of polarized and ionic species in polymerizations and related processes.

Introduction

One of the most important questions in the investigation of the ionic polymerizations is the state and participation of polarized and ionic species.

The ionogenic equilibria in organic aprotic solvents were described, e.g., by Winstein et al.(1) and Griffith and Symons (2). The amount of starting materials are known but to get information about the formed ionic and highly polarized species we have to measure both the conductivity (κ), produced by the unpaired ions, and the static permittivity (ε_0), representing the dipoles. Since both depend on the temperature (T) it is necessary to know its actual values.

The resistance and conductivity measurements and their applications in the polymer chemistry are well-known from papers of Plesch and coworkers (e.g.: 3,4) but the dielectric constant measurement has only been used in a few cases (5, and recently: 6,7).

The aim of this work was to investigate the ionogenic equilibria during a living polymerization.

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Experimental

Materials and procedures:

The materials and purification procedures have been described (8). The temperature of all chemicals was equilibrated in the bath of the dry-box before using.

To investigate the ionogenic equilibria, a specially designed instrument was developed consisting of a combined detector, measuring device and evaluation unit (9, Fig.1).

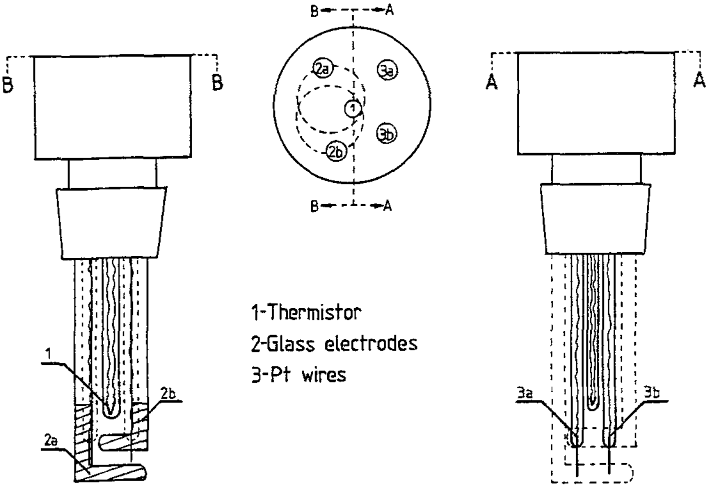


Figure 1: Scheme of the detector

The main parts of the detector are a pair of specially formed glass electrodes for capacitance (C) measurements, a pair of smooth platinum wires to measure resistance (R), and a fast thermistor. In order to reach reasonable signal/noise ratios, the head-unit converting response signals is placed directly on the top of the detector. The "active part" of the measuring device sends the 1 kHz A.C. voltage to the Pt-wires and the 100 kHz quartz-stabilized measuring impulse to the capacitance-electrodes. The "passive part" receives the D.C. signals and transforms them into the 0-10.24 Volt range which is acceptable for the 10-bits analogue/digital interface of a computer. The sampling time of the interface is 40 microseconds, thus, all type of data are measured practically simultaneously. Using a calibration, the data were evaluated by a computer-program to get values of temperature, conductivity and permittivity.

We used this instrument for monitoring the living polymerization of isobutylene (IB) initiated by the 1,3,5-tris(2-methoxy-2-propyl)benzene (TriCumOMe)/BCl_3 system (10) at -25 °C in CH_2Cl_2. The reactions were carried out in mechanically stirred 250-350 mL three-neck glass reactors in a stainless steel enclosure (dry-box) under dry nitrogen.

Three experiments were choosen to demonstrate the differences between the AMI (All Monomer In) and the aging technique. In the latter case the "reverse addition" (11) method was applied, i.e., at first the BCl_3 was introduced into the cooled solvent then the initiator was added and the polymerization was started by fast introduction of the monomer. The experimental conditions and the data of obtained polymers are shown in Table I.

Table I.: Experimental conditions and results of IB polymerizations at $-25^{0}C$ in CH_2CL_2.

Exp. No.	V [mL]	I 10^3 [mol]	BCl_3 10^3 [mol]	M 10^2 [mol]	DP/function	Technique
I	320	7.73	6.80	3.6 +10.7 +21.0	2 6 16	Aging+IMA: $(BCl_3+I)+M_1+M_2+M_3$
II	260	0.99	2.53	4.2	21	Aging: $(BCL_3+I)+M$
III	260	0.99	1.72	2.9	15	AMI: $M+I+BCl_3$

The PIB samples were quenched with prechilled MeOH, washed with 10% HCl, then with distilled water to neutrality, and dried over $CaCl_2$.

To separate the reaction steps as much as possible, in the Exp.I the IB was added in increments. In this experiment, eight 5 mL samples were taken off and transferred into a beaker containing 5 mL MeOH. To keep the reaction volume constant, 5 mL of pure precooled solvent was added after each sampling. The samples were diluted with 100 mL CH_2Cl_2 and worked up as usual.

The GPC traces were made by a Shimadzu LC-6 chromatograph, equipped with 6 Merck Hibar Lichrogel columns (PS-1, PS-4, PS-40, PS-400, PS-4000, PS-40000). The calibration was carried out with PIB standards having narrow MWD.

Results and Discussion

The representative results obtained by the direct monitoring method are shown in Figures 2, 4, and 5. The GPC traces of the obtained polymers and some samples of the Exp.I are shown in Figure 6.

All measured values of T, R and C are resultants of the simultaneous individual processes, thus a quantitative evaluation is difficult. On the other hand, the qualitative interpretation is possible and can also serve the understanding of the processes.

The basic principle of the interpretation is: if a reaction takes place in an ionic system, T, $\varkappa$ and ε_0 will change. These changes can be originated from changes in the concentration of the measured species and/or from changes of their character.

The conductivity is governed by the number of separated ions and their mobility which considerably decreases during the polymerization (12). Concerning the conductivity measure-

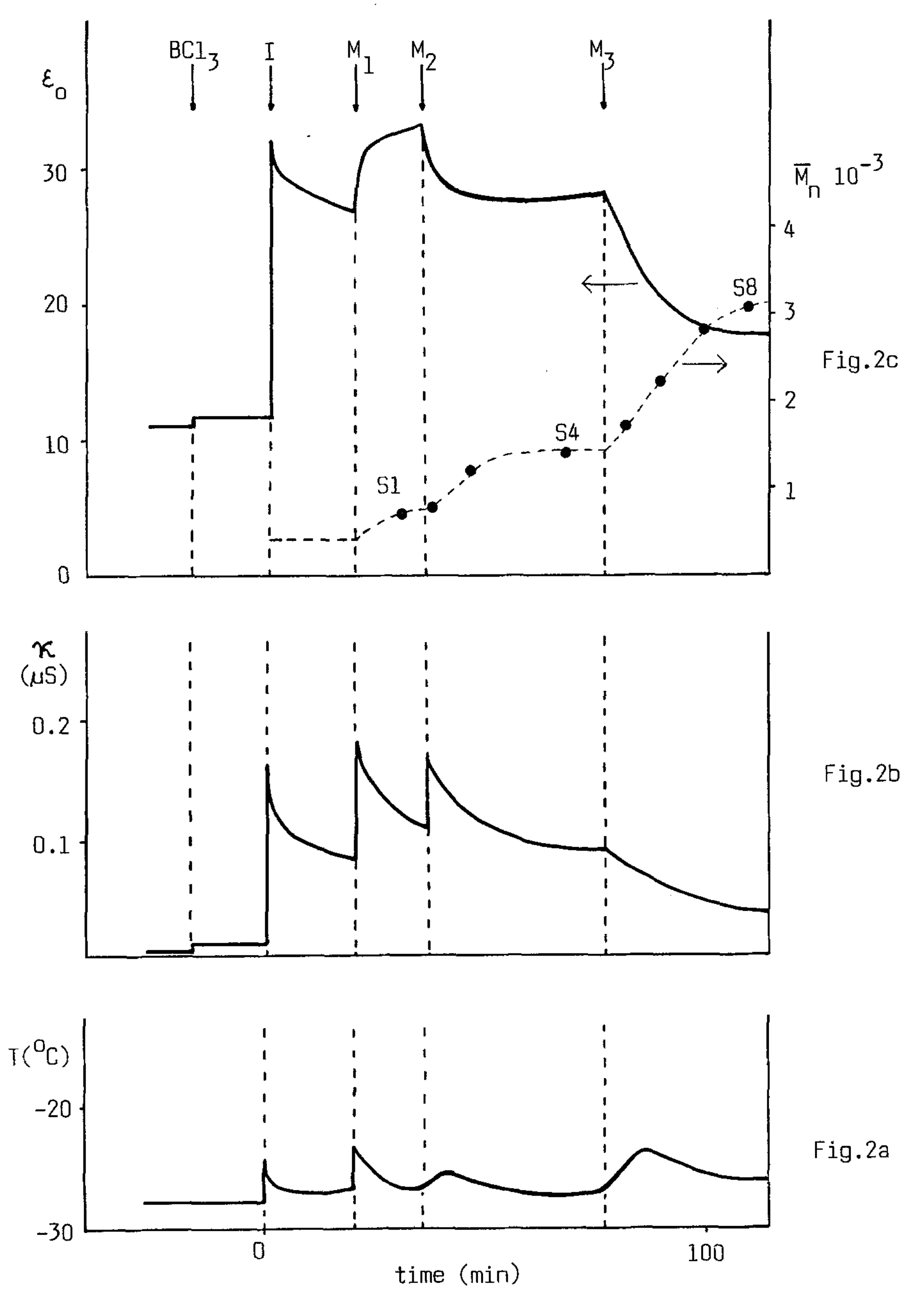


Figure 2: Time dependence of ε_0, κ and T during the polymerization of isobutylene (Experiment I).
The $\bar{M}_n$-s are measured on samples S1-S8. Final yield: 94 %, $\bar{M}_n$=3300, $\bar{M}_w/\bar{M}_n$=1.32

ment we have to emphasize that only a resultant resistance can be measured and a lot of variables may influence this value (13).

In general, if there is no specific interaction between the solvent and solute, the average dielectric constant is proportional to the molar fraction of the components (14). In the case of polymer solutions numerous other factors influence the resultant dielectric constant (14,15) and no theory of dielectric properties of living polymer solutions exist. Moreover, a permittivity measurement cannot differentiate between highly polarized species, and compact or solvent-separated ionpairs.

The change of the temperature profile (Figure 2a) suggests that the average reaction rate decreases, i.e., there are differences between the early and later stages of the polymerization.

The jumps in Figure 2b are originated from sudden rises in the concentration of the unpaired ionic species (the addition of IB accelerates the reaction with the initiator) and/or from the change of the character of the ions during the polymerization.

The average dielectric constant also changes drastically and characteristically, indicating the presence and change of strongly polarized species. (Figure 2c).

Figure 2a shows the change of the ε_0 values and the molecular weight during the reaction. When the cationation step is completed, i.e., after the second monomer addition, the average dielectric constant is inversely proportional to the molecular weight.

The ε_0 and κ values of the different samples show the same molecular weight dependence, indicating an equilibrium between the polarized species and unpaired ions during the whole polymerization (Figure 3).

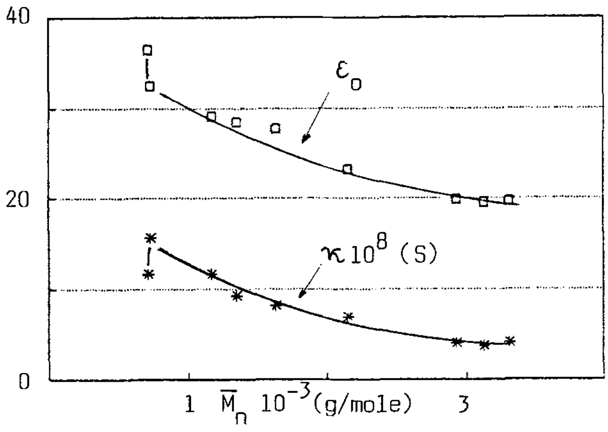
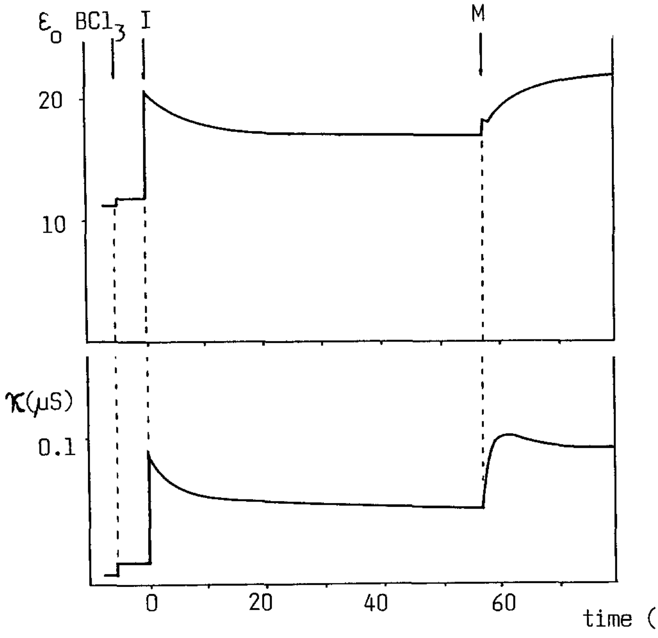


Figure 3: Comparison of the dependence of ε_0 and κ on $\bar{M}_n$

The fundamental differences between the rates and polymers (Figs. 2, 4 and 5) are that in case of Exp.III (AMI) the polymerization is fast and the polymer is monomodal, in case of Exp.II (aging) the polymerization is slow and the PIB is multimodal, while in case of Exp.I (aging+IMA) the polymerization slower than in Exp.III but faster than in Exp.II, and the MWD of the first samples is multimodal while at the end of the polymerization becomes monomodal. However,due to the slow initiation, the obtained $\bar{M}_n$ is somewhat higher than planned.



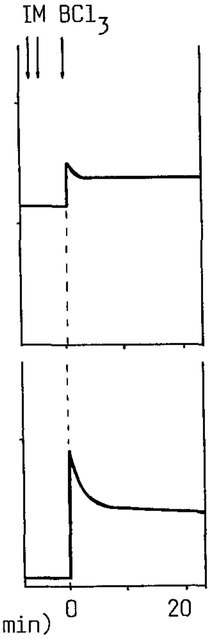


Figure 4:Time dependence of ε_0 and κ during the polymerization of isobutylene (Experiment II)

Figure 5: Same as Fig.4 in Experiment III.

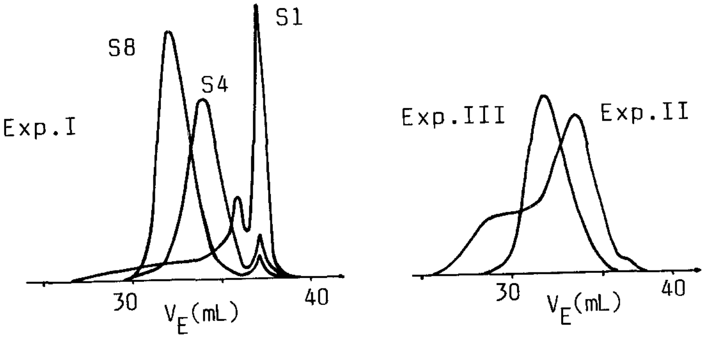
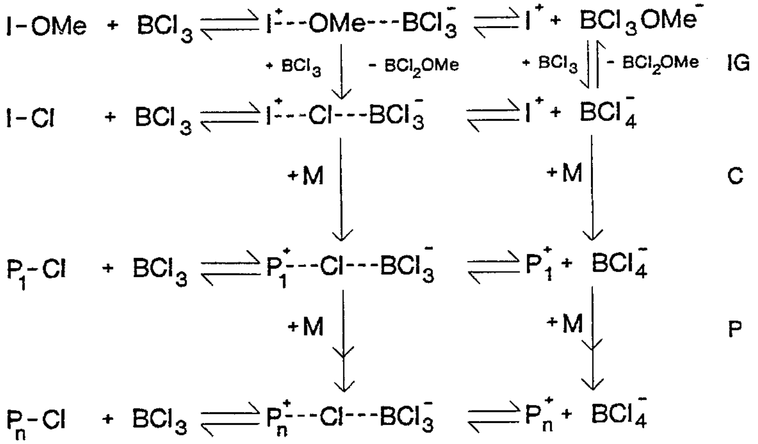


Figure 6: GPC traces of the Experiments I, II and III.

Conclusions

The presence and simultaneous change of unpaired ions and strongly polarized species confirm that ionogenic equilibria exist during the living polymerization. These changes can be interpreted by the functioning of a complex system of multi-stage dynamic equilibria between the dormant, the highly polarized and the ionic species, as shown in Scheme I.

Scheme I: Multi-stage dynamic equilibria in case of aging (monomer added after ion generation: IG). C: cationation, P: polymerization.



On the basis of this scheme we can explain why the rate of polymerization depends on the addition sequence of the reactants. Evidently, the difference is caused by the fact, that in case of aging two kinds of counterions and also methyl-dichloroboronite are formed (8). The BCl_2OMe, which is an "in situ" electron donor (16), decreases the polymerization rate. The presence of two counterions is indicated by the multimodal MWD of PIB obtained by aging as it was also recognized earlier (17) with another initiating system. The BCl_3OMe^- counterion in presence of monomer leads to very fast living polymerization (see 8) while, in the absence of monomer, the ether/chlorine exchange (18) takes place and the formed BCl_4^- results slow polymerization when monomer is added. The formed counterions, when excess BCl_3 is present, are in equilibrium with each other after the cleavage of tert.-ether bond:

$$BCl_3 + BCl_3OMe^- \rightleftharpoons BCl_4^- + BCl_2OMe$$

Of course, if we use aging, the polymerization can continue on both routes and the apparent rate of polymerization will be higher than in the case of the well-known TriCumCl/BCl_3 system (19,20).

However, using TriCumOMe initiator and starting the polymerization by the introduction of BCl_3, first the much more active BCl_3OMe^- gegenion forms, the polymerization is fast and yields monomodal PIB.

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