Bulk polymerization of isobutylene initiated by PVC/SnCl$_4$ systems

Luděk Toman* and Rudolf Lukáš

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, CS-16206 Prague 6, Czechoslovakia

Summary

It has been surprisingly discovered that an initiator system based on PVC/SnCl$_4$ produces bulk polymerization of isobutylene even under conditions, when a mixture of isobutylene and SnCl$_4$, in the absence of a polar medium, does not polymerize. The PVC polymers used were the powders of the commercial suspension PVC Neralit S-652, lower-molecular-weight PVC prepared by extraction of Neralit S-652 with acetone (PVC–AE) and the copolymer of vinyl chloride with 2-chloropropene (VC/2CP). The kinetics of polymerizations were studied dilatometrically at −78°C. It was found that the bulk polymerization of isobutylene proceeds at the boundary between the solid (PVC) and liquid (isobutylene) phase over an unusually long period of time which, depending on the type of PVC used, can last more than 7 days. It followed from the determination of the initial polymerization rate that the activity of the studied types of PVC decreases in the order PVC–AE > VC/2CP >> PVC.

Introduction

It is generally known that isobutylene does not polymerize in nonpolar medium in the presence of SnCl$_4$, even if protogenic substances, such as residual water, are present in the reaction system. The difficulty of carrying out bulk polymerization of a mixture of isobutylene and SnCl$_4$ has been described for photoinitiated polymerization (1). In this case, isobutylene did not polymerize under the action of light in the presence of SnCl$_4$ and residual water in the reaction system, even at temperatures of about −80°C. Only after several hours of irradiation of the frozen mixture of isobutylene/SnCl$_4$ at a temperature of ca. −150°C, the formation of radical-cations of the monomer was detected and these species initiated the polymerization of isobutylene after heating the mixture to −80°C. However, the yield was small, and did not correspond to more than 8% conversion (2). It is interesting in this connection that the radical-cations formed by photoinduction in the isobutylene/TiCl$_4$ (2,3) and isobutylene/VCl$_4$ (3) systems permit successful bulk polymerization and the conversions reached are higher than 80% (1). Isobutylene forms charge-transfer (CT) complexes with TiCl$_4$ (4), VCl$_4$ (4,5) and also SnCl$_4$ (4), all with a molar composition of 1:1, and these CT complexes all yield under the action of light the same radical-cation of isobutylene (2,3). Since the radical-cations of isobutylene formed in the system with SnCl$_4$ produce only small polymerization yields, it is obvious that the type of Lewis acid used probably affects the extent of the transfer and termination reactions.

*Corresponding author

We recently found that the bulk polymerization of isobutylene can be carried out in the presence of an initiation system based on PVC/BCl$_3$ (6,7). Thus, this work describes an analogous study of the properties of the PVC/SnCl$_4$ system.

Experimental

The purification and drying of isobutylene, dichloromethane, *tert*-butyl chloride (*t*-BuCl) (Fluka), and nitrogen have been described earlier (6), as well as the preparation of 2,5-dichloro-2,5-dimethylhexane (DDH) (8). SnCl$_4$ was purified by distillation. The PVC samples used were as follows: a commercial suspension type of PVC Neralit S-652 (Spolana Neratovice, Czechoslovakia), $\overline{M}_w \approx 120\,000$, $\overline{M}_n \approx 52\,000$, its acetone extract obtained at the temperature of 40°C (PVC–AE), $\overline{M}_w \approx 50\,000$, $\overline{M}_n = 31\,000$, and the copolymer of vinyl chloride with 2-chloropropene (VC/2CP), containing 5.1 mol.% of 2-chloropropene structure units, prepared by suspension copolymerization initiated by dicetyl peroxydicarbonate at 55°C, $\overline{M}_w \approx 60\,000$, $\overline{M}_n \approx 25\,000$.

The bulk polymerizations of isobutylene were carried out in dilatometers 10 ml in volume at a temperature of −78°C. At this temperature, the PVC powder was first mixed with SnCl$_4$ and then isobutylene was added. The polymerization technique employed has already been described (6,7). The polymerization conditions are given in Tables 1 and 2.

The molecular weights of the polymers were determined by GPC in THF on the HP 1084 B instrument using the universal calibration (7). Polyisobutylene (PIB) was extracted by hexane in a Soxhlet apparatus. The chlorine content in the PIB samples was determined by the Schöniger method (9).

Results and Discussion

Figure 1 depicts the conversion curves for the polymerizations of isobutylene obtained from dilatometric study of these polymerizations at a temperature of −78°C

Table 1: Bulk polymerization of isobutylene in the presence of SnCl$_4$[a]

Initiator	Conversion (%) in time								$r_o \times 10^5$
(g/l)	20 min	4 h	22 h	24 h	27 h	48 h	120 h	168 h	mol/l.s
PVC–AE 100	2.9	13.0	27.9	28.9	29.9	34.3	40.4	42.1	30.1[c] 1.1[d]
PVC–AE 50	0.5	5.1	12.6	13.5	14.4	17.8	27.1	29.7	4.8[c] 0.97[d]
VC/2CP 50	1.0	2.6	3.0	3.3	3.6	17.1	18.2	–	9.6[c] 0.32[d]
PVC 50	0.2	0.5	3.0	3.0	3.0	3.8	4.9	–	0.9[c] 0.0[c]
t-BuCl 30	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.0[c,d]
DDH 70	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.3	0.0[c,d]
H$_2$O[b]	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.0[c,d]

[a] [SnCl$_4$]$_o$ = 0.34M, $T = -78$°C, [b] residual moisture of the system, [c] in $t = 0$, [d] in $t = 24$ h
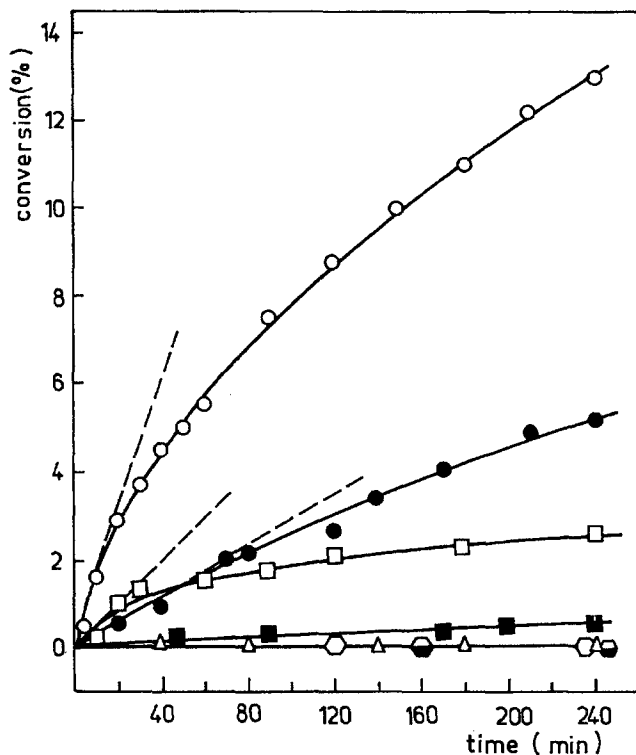
Figure 1: Conversion-time curves for the bulk polymerization of isobutylene in the presence of $SnCl_4$ initiated by ○ PVC–AE (100 g/l), ● PVC–AE (50 g/l), □ PVC, □ VC/2CP, ⬡ t-BuCl, ⬢ DDH, △ H_2O (for polymerization conditions see Table 1)

for a period of 4 hours. These curves confirm the expected nonreactivity of the t-BuCl/$SnCl_4$, DDH/$SnCl_4$, and H_2O/$SnCl_4$ initiation systems (residual water in the reaction system). However, a change in the reactivity occurs when the isobutylene/$SnCl_4$ polymerization mixture contains a powdered polymer of the PVC, PVC–AE or copolymer VC/2CP type. The presence of these powders produces the polymerization of isobutylene; it can be seen from Fig. 1 and Table 1 that the course of the polymerization is dependent on the type and amount of polymer employed. It follows from comparison of the initial rates of polymerization r_0 (Table 1) that the efficiency of the polymers decreases in the order VC/2CP > PVC–AE >> PVC. The polymerization rate is of the order of $10^{-4} - 10^{-5}$ mol/(l.s) and such low rates are unusual for isobutylene cation polymerization. On the other hand, similar r_0 values have been found for the photoinitiated polymerization of isobutylene through visible light (10).

It could be assumed that polymerization proceeding with such low rates would soon be terminated either through cation impurities present in the mixture or through collapse of the counter ions, which form a close ion pair in nonpolar medium. However, surprisingly, it was found that these polymerizations proceed over reaction times longer

than 100 hours (Table 1). It followed from comparison of the polymerization rates that, after about 30 minutes, PVC–AE becomes more active than VC/2CP and that this higher reactivity is retained throughout the polymerization (cf. the polymerization rates after 24 hours in Table 1).

A more detailed study was made of the bulk polymerization of isobutylene initiated by PVC–AE at a concentration of 100 g/l (Table 1). Figure 2 shows the distribution of molecular weights of the original sample of PVC–AE (curve 1) and the polymerization
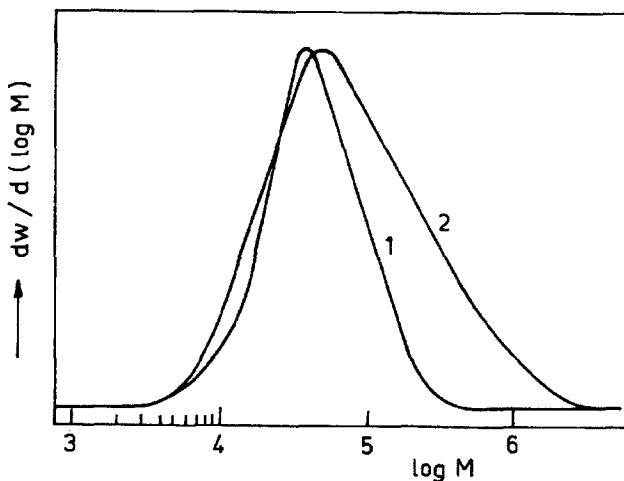

Figure 2: Molecular weight distribution of PVC–AE (curve 1) and the polymerization product containing PVC–AE and PIB (curve 2), obtained by the polymerization of isobutylene initiated by PVC–AE (100 g/l) (see Table 1)

product (curve 2), whose molecular weight $\overline{M}_w$ was about 180 000 and $\overline{M}_n \approx 41$ 000. The polymer product containing 19 wt.% chlorine was extracted with hexane in a Soxhlet apparatus for 8 hours. It was found by determining chlorine that the extracted PIB contains only traces of chlorine, while the polymer remaining after the extraction contains 56 wt.% chlorine, corresponding to the chlorine content in the PVC–AE used. It is thus apparent that the polymerization does not involve grafting onto PVC and the product, in contrast to the system co-initiated by BCl_3 (6,7), is only a mixture of PVC and PIB. Visual observation of this polymerization indicated that, after about 2–3 hours, the solid polymer particles at the bottom of the dilatometer are coated with the PIB being formed, which is insoluble in the monomer at a temperature of $-78°C$. The layer of insoluble PIB gradually grows, with simultaneous desintegration of solid PVC–AE particles. It followed from repeated experiments that the polymerization occurs at the boundary between the solid and liquid phases because no polymer or oligomer of isobutylene was found in the monomer layer. In one of these experiments, the dilatometer was carefully cut into halves after 168 hours and samples were taken from the upper, central, and lower polymer product layers. The chlorine contents in these samples, were 19, 16, and 23 %, respectively. It is thus apparent that the distribution of PVC was almost homogeneous throughout the whole

PIB volume. This fact supports our opinion (6,7) that the studied bulk polymerizations of isobutylene are also initiated inside the porous polymer particles. The polar matrix of the PVC particles most probably simulates the effect of the absent polar solvent and acts as a small polymerization reactor. It can thus be expected that the initiation activity of PVC will be affected by both the chemical structure and also the morphology, especially by the porosity of the polymer grains. In this connection, the initiation inefficiency of DDH can be explained by its insolubility in isobutylene. The crystalline DDH is impermeable for both isobutylene and $SnCl_4$ and thus the polar C−Cl bonds in DDH cannot participate in the initiation of the polymerization.

The ability of substances related to PVC to initiate polymerization of isobutylene results also from Table 2. These polymerizations were carried out in CH_2Cl_2 at −78°C
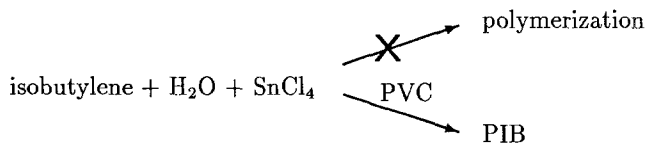
Table 2: Polymerization of isobutylene in the presence of vinyl chloride 2-chloropropene copolymer, CH_2Cl_2 and $SnCl_4$[a]

VC/2CP (g/1)	0	1	2.5	5	7.5
Conversion (%)	0	1.5	6.1	7.6	16.0

[a] $[SnCl_4]_o = 0.084M$, $[isobutylene]_o = 9M$, polymerization time 2 h, $T = -78°C$

for 2 hours at high monomer concentrations and initiated by various amounts of VC/2CP copolymer. The isobutylene conversion values obtained document the positive effect of the more polar medium and higher VC/2CP concentration on the PIB yield.

The concept that the polar PVC matrix simulates a polar medium commonly used in the polymerizations of isobutylene, e.g. in CH_2Cl_2, is interesting from the point of view of the possible polymerization mechanism. We recently found (11,12) a new initiation mechanism for the polymerization of isobutylene in CH_2Cl_2 in the presence of $SnCl_4$ and substances of the R-Cl^t type, where R-Cl^t denotes an alkyl chloride with a chlorine atom bonded to a tertiary carbon, such as t-BuCl and DDH. The results obtained led to the conclusion (11,12) that R-Cl^t does not act as an initiator in the polymerization system, but rather through the mutual interaction of R-Cl^t, $SnCl_4$ and H_2O. It rather catalytically mediates the transfer of a proton to the monomer by modified protogenic initiation. We suppose that the PVC polymers act similarly; the PVC chains also contain the structures with chlorine atoms bonded to a tertiary carbon and PVC, therefore, only mediates the protogenic initiation with residual water in the reaction system. Since a grafting reaction does not occur, PVC acts as a catalyst and not as an initiator of isobutylene polymerization. Thus, the bulk polymerization at −78°C can be described by the following scheme, where H_2O denotes residual water in the reaction system:

$$\text{isobutylene} + H_2O + SnCl_4 \quad \overset{\displaystyle \nearrow \;\; \text{polymerization}}{\underset{\displaystyle \searrow \;\; PIB}{\xrightarrow{\quad PVC \quad}}}$$

The results obtained so far lead to the following conclusions:
(a) at −78°C, PVC polymers produce bulk polymerization of isobutylene in the presence of $SnCl_4$, (b) the products of these polymerizations are not grafted copolymers and thus, the PVC polymers act only as catalysts, (c) the higher reactivity of the lower-molecular-

weight extract of PVC and of the VC/2CP copolymer indicate that the catalytic effect of the polymer particles is dependent on both the morphology and the occurrence of structural defects (alkylic and tertiary alkyl chloride structures) in the polymer chains, (d) these polymerization reactions are most probably initiated by modified protogenic initiation with residual water in the reaction system (11,12).

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