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Studies on Cationic Copolymerization of α-Methylstyrene and Indene

1. Basic Kinetic Investigations

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Summary

α-Methylstyrene (αMS) and indene (In) have been copolymerized in methylene chloride diluent using trityl ion salts, boron trifluoride methyl etherate, and trifluoroacetic acid as catalysts. Rate constants of homopolymerization of both monomers, copolymerization parameters (CPP) and "individual rate constants" (IRC) of binary first order copolymerization have been determined. The rate constants of trityl ion consumption in the presence of the monomers are qualitative measures of initiation rates. An interpretation of the differences of monomer reactivity in homopolymerization and copolymerization selectivity is proposed.

Introduction

The cationic polymerization of indene (In) and its derivatives and α-methylstyrene (αMS) has been subject of extensive investigations (SIGWALT, 1961; SIGWALT and MARECHAL, 1966; ANTON and MARECHAL, 1971; HEILBRUNN and MARECHAL, 1973; CHERADAME and VAIRON, 1966; SAUVET et al. 1969; MIZOTE et al. 1966; KUNITAKE, 1975). Both mechanistic aspects of the polymerization process and properties of the polymerization process and properties of the synthesized material have been studied. Yet, there are insufficient kinetic data for detailed investigations on reactivity and selectivity of copolymerization of the two monomers. The data reported in the literature can often not be compared because of different experimental conditions or evaluation techniques. One cannot draw conclusions on the selectivity control

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of the copolymerization by initiation and/or propagation. Recently we proposed a new method for the quantitative description of binary first order copolymerizations by determination of "individual rate constants" (IRC), i.e. k_{11}, k_{12}, k_{21}, k_{22} (HEUBLEIN and WONDRACZEK, 1981). We showed that IRC's are very convenient to predict microstructure parameters, such as diad concentration, etc., and are in this respect superior to CPP's. IRC's allowed new conclusions on "dynamics of copolymerization" of several monomer pairs (HEUBLEIN and WONDRACZEK, 1981; WONDRACZEK et al. 1982). In the course of these investigations we also studied the cationic copolymerization of α-methylstyrene and indene. The purpose of this paper is to present kinetic data for homo- and copolymerization of these monomers. By the use of different initiator systems, i.e. different initiation rates, we hoped to collect information relative to selectivity control of the copolymerization either by initiation or propagation reactions. We are aware of the complexity of initiation processes as recently reviewed (GANDINI and CHERADAME, 1980; KENNEDY and MARECHAL, 1981). We do not deal with mechanistic details of initiation, however, the assumption that the use of different initiator systems gives different initiation rates and initiation selectivities should be highly justified. Detailed investigations on copolymer microstructures will be presented later.

Experimental

Materials: Commercial indene (99 %) and commercial α-methylstyrene (99 %) were purified by the usual methods and distilled twice under dry argon atmosphere from CaH_2 and immedeately used for polymerizations. Bromobenzene was distilled from P_2O_5 and subsequently from CaH_2 under dry argon and used as internal standard for quantitative GC analyses of monomer concentration during polymerizations. Methylene chloride (99%) was purified by the usual methods and subsequently distilled twice each from P_2O_5 and CaH_2 under dry argon atmosphere. After this procedure the water content was below the detection limit of Karl-Fischer titration ($\ll$ 1 mM).

$BF_3O(CH_3)_2$ (Ferrak) was purified by fractional distillation. CF_3COOH (Merck) was used without further purification. Ph_3CSbCl_6 was prepared by reacting trityl chloride with $SbCl_5$ in $CHCl_3$. After recrystallization from dry dichloroethane it was dried in vacuo. Ph_3CBF_4 and PH_3CPF_6 (Fluka) and Ph_3CAsF_6 and Ph_3CSbF_6 (Ventron) were dried in vacuo and used without further purification.

Polymerizations: All polymerizations were carried out under dry argon atmosphere in specially designed baked out glass reactors with a double mantle for external cooling by a cryostate. The reactor was charged with solvent, monomer and internal standard. The mixture was stirred at 258 K by a magnetic stirrer. The polymerization was then started by direct introduction of initiator solutions in methylene chloride through a silicon rubber septum using baked out syringes. Monomer conversion was determined by gaschromatography (composition analysis of the feed). Polymerizations were terminated by addition of CH_3OH.

Results and Discussions

TABLE 1 shows overall rate constants of cationic polymerizations of α-methylstyrene (k_α) and indene (k_{In}) using different initiator systems. The CPP, r_1 and r_2, (M_1 = αMS) have been determined for copolymerizations of both monomers under the same experimental conditions by a nonlinear calculation method from monomer feed compositional analysis data (HEUBLEIN et al. 1976 a).

TABLE 1

Homo- and Copolymerization of αMS and In by Various Initiator Systems (CH_2Cl_2 at 258 K, [M] = 0,5 mM, [αMS]/[In] = 1:2)

No.	Initiator system		$k_\alpha x\ 10^4/s^{-1}$	$k_{In}\ x\ 10^4/s^{-1}$
1	Ph_3CBF_4	5 mM	1.27 ± 0.10	0.08 ± 0.002
2	Ph_3CAsF_6	5 mM	0.73 ± 0.07	0.06 ± 0.02
3	Ph_3CPF_6	5 mM	1.63 ± 0.08	0.20 ± 0.06
4	Ph_3CSbF_6	5 mM	3.95 ± 0.11	0.15 ± 0.04
5	Ph_3CSbCl_6	5 mM	12.20 ± 0.10	0.67 ± 0.20

No.	Initiator system	$k_{\alpha} x 10^4/s^{-1}$	$k_{In} x 10^4/s^{-1}$
6	$BF_3.OMe_2$ 5 mM	1.10 ± 0.05	0.03 ± 0.02
7	CF_3COOH 500 mM	93.9 ± 7.0	1.72 ± 0.01
8	CF_3COOH 250 mM	26.6 ± 5.4	0.29 ± 0.04
9	CF_3COOH 100 mM	2.6 ± 0.01	no polymn.

No.	k_{α}/k_{In}	r_1	r_2	r_1/r_2
1	15.9 ± 1.3	2.9 ± 0.11	0.48 ± 0.008	6.04 ± 0.25
2	12.2 ± 4.2	3.1 ± 0.14	0.48 ± 0.01	6.46 ± 0.32
3	8.15± 2.5	3.2 ± 0.42	0.48 ± 0.02	6.67 ± 0.91
4	26.3 ± 7.1	2.3 ± 0.15	0.48 ± 0.025	4.8 ± 0.4
5	17.9 ± 5.4	1.6 ± 0.14	0.35 ± 0.013	4.57 ± 0.43
6	36.7 ± 24.0	3.8 ± 0.3	0.45 ± 0.01	8.44 ± 0.69
7	54.6 ± 4.1	3.0 ± 0.7	0.68 ± 0.04	4.41 ± 1.1
8	88.3 + 22.0	n.d.	n.d.	n.d.
9	n.d.	n.d.	n.d.	n.d.

We consider the value of k_{α}/k_{In} as a measure of the apparent monomer reactivity ratio under the given reaction conditions, whereas the ratio r_1/r_2 refers to a selectivity parameter of the copolymerization (HEUBLEIN et al. 1976 b); i.e. the larger r_1/r_2 the more preferred is the consumption of M_1. Copolymerization selectivity obviously is much lower than expected from apparent monomer reactivity ratios (compare columns 6 and 9 in TABLE 1). In other words, the less reactive monomer indene (In) is consumed faster in copolymerization than in homopolymerization.

TABLE 2 presents characteristic data of the stable trityl ion salts. K_D are dissociation constants determined by conductivity measurements (CH_2Cl_2 at 298 K), k_{TC} are spectroscopically determined rate constants of trityl ion consumption by interaction with monomers (CH_2Cl_2 at 298 K). It has to be emphasized again that we have no evidence on details of this interaction of the two olefins with trityl ions in the presence of traces of moisture. Under our experimental conditions ($[H_2O] < 1$ mM, $[Ph_3CMtX_{n+1}]$ ca. 0.05 mM, $[M] = 80$ mM), however, the intensity of characteristic trityl ion absorption (410 nm) in pure CH_2Cl_2 remained constant over a period of several hours. Therefore, fast trityl ion consumption by reaction with residual water in the solvent can be excluded. Only upon monomer addition did the trityl ion absorption rapidly disappeare. A first order evaluation of the obtained kinetic curves was employed to calculate k_{TC}. The k_{TC}'s are regarded to be rough measures of initiation rates of cationic polymerizations of αMS and In, respectively, in the presence of trityl ion salts as initiators.

TABLE 2

Characteristic Data of Trityl Ion Salts

$MtX_{n+1}^{\ominus}$	$10^4K_D/mol.l^{-1}$	$10^4k_{TC}(\alpha MS)/s^{-1}$	$10^4k_{TC}(In)/s^{-1}$
$BF_4^{\ominus}$	1.7	4.16 ± 0.11	3.68 ± 0.23
$AsF_6^{\ominus}$	2.0	0.74 ± 0.06	0.42 ± 0.09
$PF_6^{\ominus}$ +)	n.d.	n.d.	n.d.
$SbF_6^{\ominus}$	2.1	6.62 ± 0.23	2.38 ± 0.31
$SbCl_6^{\ominus}$	2.1	10.8 ± 0.86	4.20 ± 0.24

+) very unstable in the presence of light and water

Data in TABLE 1 and TABLE 2 prove that there is a correlation between rate constants of initiation (represented by k_{TC}) and overall polymerization rate constants (k_α and k_{In}). Evidently, both are in the same order of magnitute when stable trityl ion salts are used as initiators. Thus, the overall rate constants seem to depend strongly on the initiation process; i.e. initiation appears to be rate controlling. Furthermore, k_α and $k_{TC}(\alpha MS)$ are almost equal in most systems whereas $k_{TC}(In)$ is much higher than k_{In} in each case. The interaction of the monomer with the trityl ion salt, as represented by the k_{TC} data, seems to play an important role in the initiation step but does not describe the entire process. The nature of this interaction still remains unclear (GANDINI and CHERADAME, 1980).

The IRC's of the copolymerization of a 1:1 mixture of MS(M_1) and In(M_2) using Ph_3CBF_4 initiator are $k_{11} = (1.2 \pm 0.2) \cdot 10^{-4}s^{-1}$, $k_{12} = (0.76 \pm 0.06) \cdot 10^{-4}s^{-1}$, $k_{21} = (0.89 \pm 0.02) \cdot 10^{-4}s^{-1}$, $k_{22} = (0.56 \pm 0.09) \cdot 10^{-4}s^{-1}$. It is obvious that the αMS consuming processes (k_{11} and k_{21}) exhibit similar rate constants as k_{α} of homopolymerizations, whereas the In consuming processes (k_{22} and k_{12}) are much faster in copolymerization than in homopolymerization (see line 1 in TABLE 1). Similar results are obtained in other systems. From the IRC's "teoretical" CPP's can be calculated:
$r_1(th) = k_{11}/k_{12} = 1.6 \pm 0.3$, $r_2(th) = k_{22}/k_{21} = 0.63 \pm 0.1$.
The "kinetic" CPP's have been determined in the usual way (HEUBLEIN et al 1976 a):
$r_1(kin) = 2.2 \pm 0.3$, $r_2(kin) = 0.89 \pm 0.03$
The related selectivity parameters are almost identical for both data pairs: $r_1/r_2(th) = 2.54 \pm 0.62$ and $r_1/r_2(kin) = 2.47 \pm 0.35$. Thus, the selectivity of monomer consumption is sufficiently well described by the kinetic CPP's. For the copolymerization of αMS and isobutylene, however, we showed that the copolymer microstructure (sequence length distribution) can be calculated far more precisely by means of IRC than by CPP (HEUBLEIN and WONDRACZEK, 1981; WONDRACZEK et al. 1982).

The apparently higher reactivity of In in copolymerization with αMS than in In homopolymerization (see TABLE 1) seems to support the assumption that cationic In polymerization might be initiation controlled; i.e., the generation of a propagating carbenium ion from In using trityl ion salts, BF_3OMe_2 or CF_3COOH as catalysts, is a slow process. In a copolymerization system where the propagating carbenium ions are mainly generated from another monomer (αMS), however, In exhibits apparently higher reactivity. These observations lead to the conclusion that the selectivity of cationic copolymerization in this case may be at least partially controlled by a selective initiation.

TABLE 1 also shows that different initiating systems lead to different copolymerization selectivities. Within this series of experiments the r_1/r_2 selectivity parameters follow the order Lewis acid > carbenium ion salt > protic acid. Surprisingly, the lowest selectivity parameters are found in the case of CF_3-COOH and Ph_3CSbCl_6 where large differences in apparent monomer reactivity are observed. The parameter r_1/r_2 refers only to comonomer consumption. More detailed information can be provided by precise microstructure analyses as presented in a futurel paper.

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