## Structure-Property Dependence of Copolymers Prepared by Cationic Polymerization

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## ABSTRACT

$\alpha$-Methylstyrene/isobutene, $\alpha$-methylstyrene/diisobutene, cyclopentadiene/isobutene, and cyclopentadiene/$\alpha$-methylstyrene were copolymerized by cationic polymerization techniques. Several properties of the copolymers such as softening ranges and oxidation stability depend on their constitutional composition, and were controlled by variation of the conditions of their synthesis.

## INTRODUCTION

Copolymers made from isobutene (IB), diisobutene (DIB), cyclopentadiene (CPD), and $\alpha$-methylstyrene ($\alpha$-MeSt) are of interest for different uses, e.g., for resins, adhesives, and mineral oil additives. Therefore, we have investigated these copolymers which should be easily available by cationic polymerization initiated by Lewis acids in the presence of small amounts of water ($10^{-3}$ mol/L).

By investigating the cationic copolymerization of $\alpha$-MeSt and IB initiated by Lewis acids, we have found that the chemical homogenity and the sequence-length distribution of the copolymers depend remarkably on the reaction conditions [1, 2]. Similar results were obtained in the copolymerization of CPD and IB [1] and in the copolym-

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erization of CPD and α-MeSt [3]. As expected, the thermal stability of poly(α-MeSt-co-IB) improves on increasing the content of IB units. This is caused by the interruption of the zip mechanism of the thermal depolymerization of poly(α-MeSt) [2].

The relative high tendency to oxidized of poly(CPD) and of copolymers containing CPD can be suppressed when the copolymerization technique employed generates a random distribution of monomer units in the polymer chain, as shown previously [3].

## RESULTS AND DISCUSSION

The copolymerization of α-MeSt and DIB, mainly consisting of 2,4,4-trimethylpentene-1 (TMP-1), should result in products comparable with poly(α-MeSt-co-IB), and offers an easier technological procedure by using two liquid monomers. Table 1 shows the dependence of the monomer conversion and the copolymer composition on the reaction conditions.

The conversion was estimated by GC analysis of the monomers remaining in the feed. The copolymer composition was determined by ^{1}H-NMR-spectroscopy after extraction of the total product with n-pentane.

Table 2 contains the copolymer composition, the softening range, and the average molecular weight of the extracted copolymers. Although the DIB content of the copolymers obtained is lower than the IB content in poly(α-MeSt-co-IB), the thermal stability (decomposition between 600 and 650 K) remains comparable. The molecular weight, however, drops within the ratio 10:1, obviously caused by the lower reactivity of DIB and the tendency to undergo transfer reactions. Moreover, the softening range of poly(α-MeSt-co-DIB) is also decreased.

According to our paper on the copolymerization of CPD and IB, we calculated so-called "individual rate constants" (IRC) from the concentration-time curves [1], and obtained the following results for $M_1$ = CPD and $M_2$ = IB:

$$k_{11} = 1180.00 \times 10^{-5} \ s^{-1}$$
$$k_{12} = \phantom{00}71.30 \times 10^{-5} \ s^{-1}$$
$$k_{21} = \phantom{000}8.95 \times 10^{-5} \ s^{-1}$$
$$k_{22} = \phantom{000}1.00 \times 10^{-5} \ s^{-1}$$

The higher relative reactivity of CPD results in longer sequences within the poly(CPD-co-IB), at least during the first stage of the reaction. The k values agree well with sequence-length distribution analysis by ^{1}H-NMR [1]. Further evidence was found in investigations of the copolymerization of CPD and IB initiated by $Et_3Al/t$-BuCl in

TABLE 1. Dependence of the Monomer Conversion and the Copolymer Composition on the Reaction Conditions in the Copolymerization of $\alpha$-MeSt and DIB[a]

| Initiator | Initiator concentration × $10^3$ (mol/L) | Temperature (°K) | $\alpha$-MeSt conversion (%) | DIB conversion (%) | mol% DIB[b] (total product) | mol% DIB[c] (after extraction) |
|---|---|---|---|---|---|---|
| $BF_3 \cdot OEt_2$ | 3.9 | 253 | 57.3 | 0.9 | 1.5 | - |
| $BF_3 \cdot OEt_2$ | 3.9 | 223 | 9.5 | 0.8 | 7.8 | - |
| $BF_3 \cdot OEt_2$ | 3.9 | 195 | 0.4 | 0 | 0 | - |
| $BF_3 \cdot OEt_2$ | 7.8 | 293 | 98.3 | 32.4 | 24.8 | 9.8 |
| $AlEt_2Cl/t\text{-}C_4H_9Cl$ | 7.8 | 293 | 99.0 | 48.7 | 32.8 | 18.0 |
| $F_3CCOOH$ | 800 | 293 | 97.8 | 59.1 | 37.7 | 22.9 |

[a]Other conditions: $CH_2Cl_2$, 52 mL; $\alpha$-MeSt, 0.9 mol/L; DIB, 0.9 mol/L (90 mol% TMP-1).

[b]Calculated from residual monomer analysis by GC (internal standard: bromobenzene 0.9 mol/L).

[c]Detected by $^1$H-NMR-spectroscopy after extraction with n-pentane.

TABLE 2. Influence of the Reaction Conditions on Conversion, Copolymer Composition, and Molecular Weight in the Copolymerization of $\alpha$-MeSt and DIB[a]

| Initiator | Temperature (°K) | Yield (%) | mol% DIB (after extraction) | $M_n$ (g/mol) | Softening range (°K) |
|---|---|---|---|---|---|
| $AlBr_3$ | 263 | 70.5[b] | 5.5 | 1000 | 366-371 |
| $AlBr_3$ | 243 | 26.3[b] | 0.7 | 1600 | 405-411 |
| $AlBr_3$ | 273 | 57.6[b] | 15.3 | 700 | 315-318 |
| $AlBr_3$ | 253 | 76.7[b] | 1.9 | 1500 | 401-407 |
| $AlEt_2Cl/t$-$C_4H_9Cl$ | 263 | 89.5[c] | - | 700 | 310-313 |
| $TiCl_4$ | 263 | 38.9[c] | - | 700 | 323-329 |
| $SbCl_5$ | 263 | 30.0[c] | - | 400 | - |
| $Al_2Et_3Cl_3$ | 263 | 90.2[c] | 23.9 | - | - |
| $AlBr_3$ | 303 | 66.0[c] | 22.0 | 300 | - |
| $AlCl_3$ | 263 | 35.6[c] | - | 500 | - |
| $AlEt_2Cl/t$-$C_4H_9Cl$ | 233 | 66.0[b] | - | 2400 | - |
| $AlEt_2Cl/t$-$C_4H_9Cl$ | 233 | 79.5[c] | - | 800 | 325-332 |
| $BF_3 \cdot OEt_2$ | 263 | 45.0[c] | 0.1 | 1000 | 381-390 |

[a]Other: $CH_2Cl_2$, 60 mL; $\alpha$-MeSt, 0.175 mol/L; DIB, 0.075 mol/L ($\sim$80% TMP-1). Initiator: $2.4 \times 10^{-4}$ mol/L.
[b]Precipitated in $CH_3OH$.
[c]Total product, oligomers included.

TABLE 3. Influence of the Starting Monomer Ratio on Yield, Copolymer Composition, and Degree of Isomerization in the Copolymerization of CPD and IB[a]

| Monomer ratio | | Yield (%) | CPD content in monomer feed (mol%) | CPD content in the copolymer (mol%) | Degree of isomerization (%) |
|---|---|---|---|---|---|
| CPD | IB | | | | |
| 1 | 0 | 100 | 100 | - | - |
| 5 | 1 | 84 | 83.5 | 90 | 5 |
| 3 | 1 | 83 | 75 | 81 | 10 |
| 1 | 1 | 81 | 50 | 56 | n.d. |
| 1 | 2 | 77 | 33.5 | 43 | 36 |
| 1 | 3 | 65.5 | 25.0 | 36 | 43 |
| 1 | 5 | 62 | 16.5 | 31 | 63 |
| 1 | 9 | 25 | 11.1 | 30.5 | 95 |
| 0 | 1 | 13.4 | - | - | - |

[a]Reaction conditions: Total monomer concentration = 1 mol/L; $Et_3Al$ = 2.5 × $10^{-3}$ mol/L; t-BuCl = 0.5 × $10^{-2}$ mol/L; 195 K; solvent = $CH_2Cl_2$; time: 30 min.

methylene chloride solvent at 195 K. Yield, copolymer composition, and degree of isomerization of cyclopentadiene units in the copolymer are listed in Table 3.

The degree of isomerization obtained by ^{1}H-NMR spectroscopic analysis of the copolymers is defined as the ratio of normally expected 1,2- and 1,4-linked units to 1,1- and/or 1,3-units [1].

Table 3 indicates an increasing degree of isomerization with decreasing CPD concentration in the feed. This finding suggests the role of monomer solvation as a stabilizing factor of the propagating species with the "weak" cyclopentadienyl cation which is preferably solvated by the "weak" CPD. The energy of activation for the propagation step should be lower in this case because of the interaction between the cyclopentadienyl cation and the "hard" $\pi$-donor IB. Therefore, the formation of CPD sequences without isomerization seems reasonable. In the case of "weak-hard" interaction, isomerization is a fast stabilizing step prior to propagation and results predominantly in isomerized CPD units in the copolymer. Generally, this behavior can be expected in the copolymerization of monomers with large differences in their relative reactivities.

An additional confirmation of this suggestion is given by the fact

TABLE 4. Time-Dependent Monomer Conversion and Copolymer Composition in the Copolymerization of CPD and $\alpha$-MeSt[a]

| Time (min) | CPD conversion (%) | $\alpha$-MeSt conversion (%) | CPD content of the copolymer (%) |
|---|---|---|---|
| 1 | 81.4 | 62.8 | 56.7 |
| 3 | 92.7 | 71.3 | 56.3 |
| 5 | 94.2 | 74.0 | 55.9 |
| 20 | 100 | 88.0 | 53.2 |
| 60 | – | ~100 | – |

[a]Reaction conditions: Toluene = 42 mL; CPD = 0.775 mol/L; $\alpha$-MeSt = 0.775 mol/L; $TiCl_4$ = 2.5 × $10^{-2}$ mol/L; $AlBr_3$ = 4.1 × $10^{-4}$ mol/L; 253 K.

that copolymers obtained by different monomer addition techniques are not stable against oxidation and behave like poly(CPD), which is caused by long CPD sequences.

Improved oxidation stability of the copolymers was found when CPD was copolymerized with $\alpha$-MeSt using $TiCl_4$/$AlBr_3$ as the initiating system (60:1) in toluene solvent at 253 K [3].

Table 4 shows the time-dependent conversion of the monomers as determined by GC analysis of residual monomers. Obviously, CPD is the more reactive monomer but the reactivity difference is lower than in the CPD/IB system. The different ability of the propagating cations toward resonance stabilization may be illustrated by comparing the $pK_{BH^+}$ values [4] which are

| | |
|---|---|
| Cyclopentadienyl cation: | 8.7 |
| Cumyl cation: | 7.4 |
| t-Butyl cation: | 15.5 |

Therefore, it can be expected that the similar relative reactivities in the CPD/$\alpha$-MeSt system result in more randomly distributed monomer units in the copolymer, particularly if the total concentration of the monomers is very low. Then the difference in the monomer solvation of the growing species should be negligible.

Table 5 shows copolymerization data obtained after continuous addition of the monomer mixture to the dissolved initiating system.

The CPD content of poly(CPD-co-$\alpha$-MeSt) can be varied by changing the CPD concentration in the feed. After termination of polymerization by the addition of methanol, and after twofold reprecipitation of the crude product in $CH_2Cl_2$/$CH_3OH$, the copolymers of different CPD

TABLE 5. Variation of Monomer Feed in the Copolymerization of CPD and $\alpha$-MeSt, Applying the Batch Technique[a]

| CPD concentration in feed (mol%) | Yield (%) | CPD content of the copolymer (%) | $M_n$ (g/mol) |
|---|---|---|---|
| 83.3 | 91.7 | 83.2 | 2700 |
| 75.0 | 88.9 | 75.5 | 2500 |
| 66.7 | 87.6 | 68.5 | - |
| 50.0 | 88.4 | 60.3 | 2400 |
| 25.0 | 76.3 | 31.0 | 2200 |

[a]Reaction conditions: Xylene = 42 mL; CPD + $\alpha$-MeSt = 1.55 mol/L; $TiCl_4$ = $5 \times 10^{-2}$ mol/L; $AlBr_3$ = $8.2 \times 10^{-4}$ mol/L; 283 K.

content were quite stable with regard to oxidation. For example, 1 g of poly(CPD-co-$\alpha$-MeSt) containing 50 mol% of CPD only increases by 3 mg in weight when exposed to air for one year. It remained soluble in methylene chloride and other solvents.

We believe that similar monomer reactivities and the polymerization technique employed (continuous addition of the monomer mixture to the initiating system solution) lead to a random distribution of the monomer units in the polymer chain. Therefore, the sensibility toward oxidation of the copolymers is remarkably lowered compared with that of long CPD sequences.

Finally, we point out that the properties of copolymers depend not only on the overall composition but also strongly depend on the sequential composition of the product. Particularly, cationic copolymerization performance at low total monomer concentrations leads to a time-dependent sequential composition. The resulting chemical inhomogenity apparently produces some physical inhomogenity, and in this way changes the properties of the product.

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