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'Living' cationic copolymerization of isobutyl vinyl ether with methyl vinyl ether: copolymerization parameters and properties of the copolymers

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Abstract: The copolymerization of isobutyl vinyl ether (IBVE) with methyl vinyl ether (MVE), initiated by the system 1,1-diethoxyethane/trimethylsilyl iodide/zinc iodide and conducted at 0°C in toluene, was found to be 'living' just as the homopolymerizations of these monomers. Monomer reactivity ratios are $r_{\mathrm{IBVE}} = 1.08$ and $r_{\mathrm{MVE}} = 0.43$. The lower critical solution temperature of polyMVE in water, situated around 37°C, was lowered to 10°C (for a 0.25 wt.-% solution) when 6 mol-% of IBVE units were introduced in copolymers of molar mass 3000 - 7000 g/mol. At higher IBVE contents, the polymers are insoluble in water at all temperatures.

Introduction

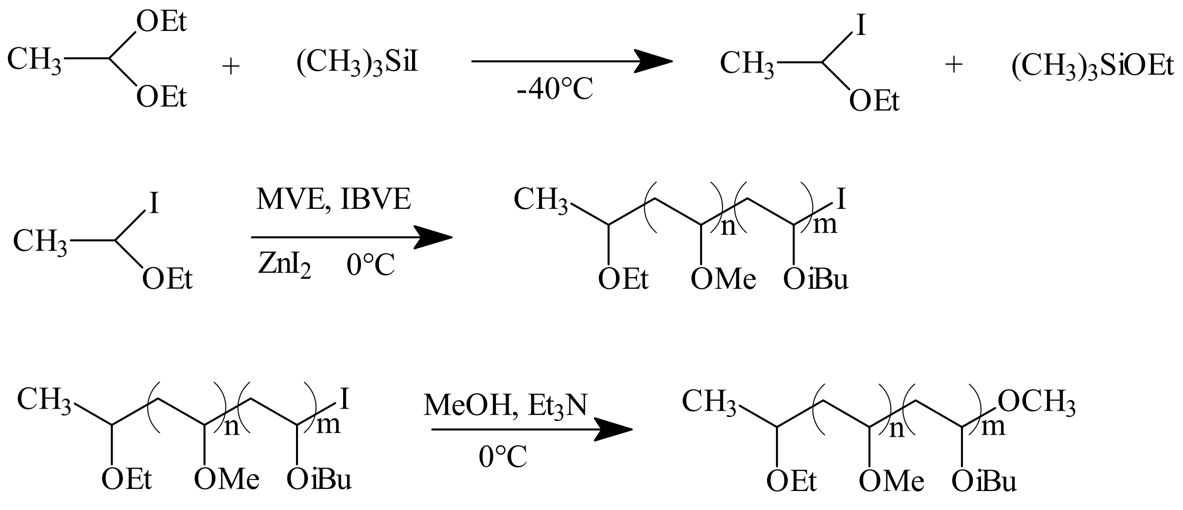
The living cationic polymerization of vinyl ethers is now a well-established method for the synthesis of well-defined end group functionalized polymers [1-3]. However, few random copolymerizations of vinyl ethers under conditions suitable for living polymerization have been studied until now [4-7]. Copolymers formed by living mechanisms may lead to random copolymers if the reactivity ratio parameters are close to unity but may lead to 'gradient' copolymer structures if the reactivity ratios are very different. In the present paper, the copolymerization of isobutyl vinyl ether (IBVE) with methyl vinyl ether (MVE) is described.

PolyMVE is a polymer that is water-soluble at low temperatures, but becomes insoluble above a lower critical solution temperature (LCST) which is situated at approx. 37°C [8-14]. In the study presented here, the influence of the incorporation of IBVE units on the LCST of polyMVE was studied.

Results and discussion

Polymerizations

The (co)polymerizations were carried out in toluene at 0°C with the initiating system trimethylsilyl iodide/1,1-diethoxy ethane/zinc iodide (TMSI/DEE/ZnI_2), which is known to produce living vinyl ether polymerizations [15,16]. For the termination, methanol was used, containing triethylamine as a proton trap. Thus, the complete reaction sequence is as follows:



Copolymer composition

^1H NMR spectra of polyIBVE, polyMVE and poly(IBVE-*co*-MVE) are presented in Fig. 1. The spectrum of poly(IBVE-*co*-MVE) shows the absorption bands of both polyIBVE and polyMVE, indicating the successful copolymerization of the two monomers.

The compositions of the copolymers were obtained from their ^1H NMR spectra using integration of the CH_3 (f) peak, characteristic of IBVE units, the CH_2 (e, c) peak, characteristic of IBVE and MVE units, and peak i originating from the initiator and assuming that initiation by DEE was quantitative. This assumption is confirmed by comparison of the integration of the terminal acetal peak (a), corresponding to 1 proton, with the integration of the initiator end group (i), corresponding to 6 protons, which is in good agreement with the expected ratio $i : a = 6 : 1$.

The number of IBVE units m is given by $m = f / i$, where f is the area of the signal at 0.9 ppm (peak f) corresponding to 6 protons of the isobutyl groups.

The number of MVE units n is given by $n = (6A - 3f) / 2i$, where A is the area of the signals between 1.4 - 1.9 ppm corresponding to 2 protons of MVE (c) and 3 protons of IBVE (c, e).

The fraction of IBVE in the copolymer is then given by $X_{IBVE} = m / (m + n) = 2f / (6A - f)$.

Livingness

The composition, molar mass and polydispersity of copolymers obtained from different monomer feed compositions with a $[M]_o / [I] = 100$ and isolated after 4 h polymerization, are summarized in Tab. 1. It was observed that, for polymerizations with high MVE fraction, considerably higher amounts of the activator (ZnI_2) were necessary to ensure high conversions, compared to polymerizations with low MVE fraction. This is believed to be due to the higher tendency of ZnI_2 to complexation of MVE and/or PMVE compared to IBVE and/or PIBVE.

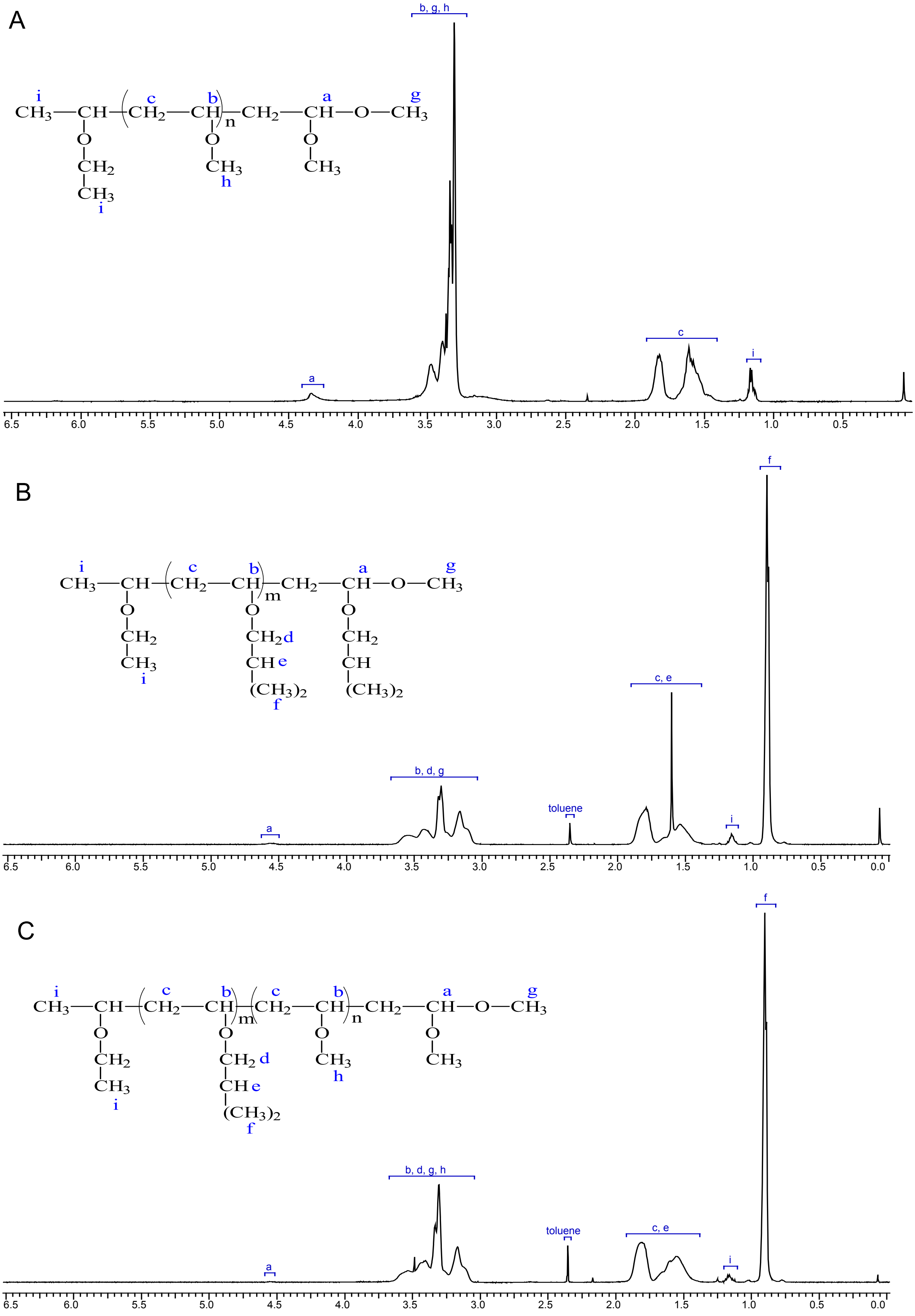


Fig. 1. ^{1}H NMR spectra of polyMVE (A), polyIBVE (B) and poly(IBVE-*co*-MVE) with 44/56 ratio (C) in CDCl$_3$

Values of M_n, obtained from gel permeation chromatography (GPC), are systematically somewhat higher than those determined from ^1H NMR analysis, especially for copolymers with high MVE content. This is attributed to the fact that polystyrene was used as standard for GPC calibration. The values obtained from NMR are in reasonable agreement with the values calculated assuming fast and quantitative initiation followed by living copolymerization. The polydispersities of the copolymers are lower than 1.16, which is in accordance with a living polymerization mechanism.

Tab. 1. Copolymerization of IBVE and MVE: molecular weight and polydispersities of copolymers obtained after 4 h

IBVE/MVE mole ratio	$[I]_0/[A]_0$ [a]	Yield [b] in %	m/n [c]	DP_n [d]	M_n		M_w/M_n [f]
					^1H NMR	GPC [e]	
10/90	10	70	11/54	65	4 310	5 050	1.16
20/80	10	72	16/50	66	4 580	5 250	1.12
30/70	10	75	23/45	68	4 990	5 500	1.16
40/60	10	74	31/39	70	5 440	5 900	1.08
50/50	20	80	40/33	73	6 000	6 400	1.08
60/40	40	79	55/24	79	6 970	7 250	1.06
70/30	50	86	65/18	83	7 620	7 950	1.04
80/20	100	91	74/14	88	8 290	8 500	1.06
90/10	100	98	89/7	96	9 390	9 550	1.07

[a] $[DEE]_0/[ZnI_2]_0$. [b] Yield = end weight / theorical weight, calculated for complete conversion of both monomers. [c] m: PIBVE units, n: PMVE units; values determined by ^1H NMR. [d] Total degree of polymerization with DP_n = m + n. [e] Calibrated by polystyrene standards. [f] Determined by GPC.

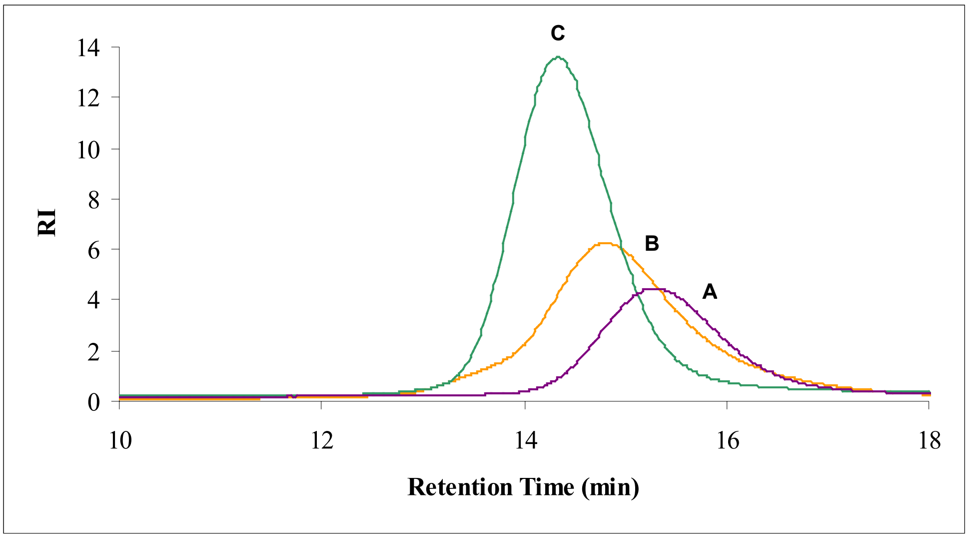


Fig. 2. GPC analyses in $CHCl_3$ of a poly(IBVE-*co*-MVE), IBVE/MVE = 44/56, after 15 min (A), after 1 h (B), and after 4 h (C)

Samples were taken from the reaction mixture after increasing reaction times and analysed by GPC and ^{1}H NMR. GPC analysis showed an increase in molecular weight as a function of time and a narrow molecular weight distribution (Fig. 2). The straight line in Fig. 3 shows that the degree of polymerization increases linearly with conversion, which is in agreement with the living character of the polymerization.

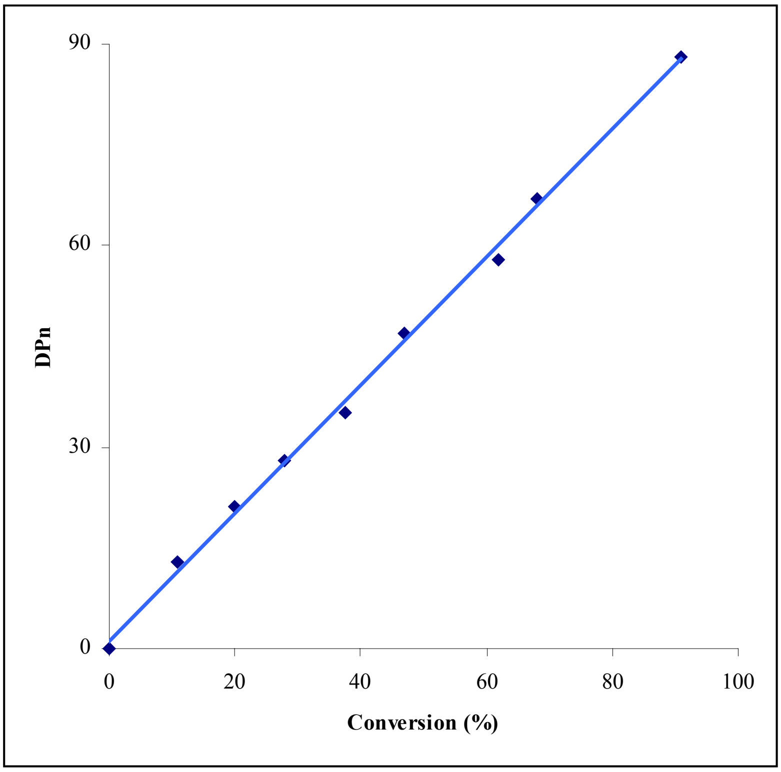


Fig. 3. Degree of polymerization of poly(IBVE-*co*-MVE) as a function of conversion

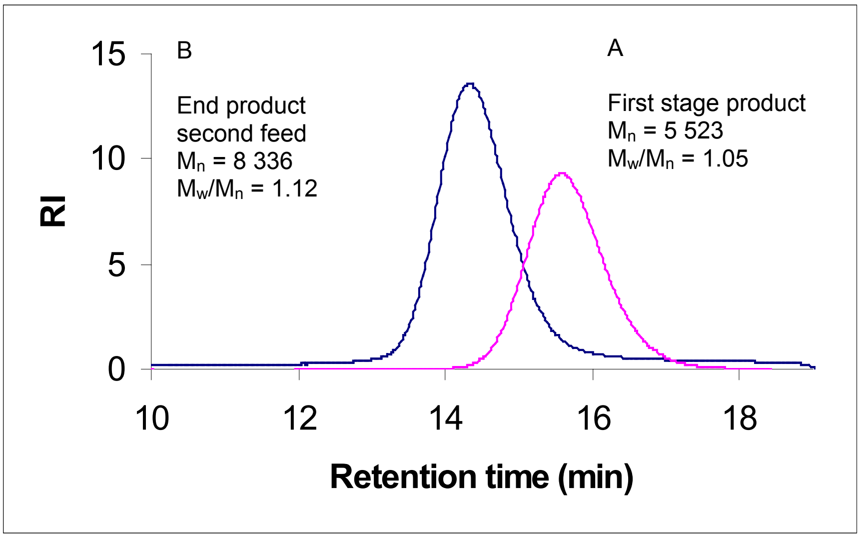


Fig. 4. GPC results of two-stage copolymerization with IBVE/MVE ratio of 30/70 performed at 0°C in toluene. Second monomer addition 3 h 30 min after initiation of the first polymerization

To further confirm the living nature of the copolymerization under the conditions used, a second monomer feed was added to the reaction mixture after a quantitative firststage polymerization. The number-average molecular weight of the end product had increased in proportion to the freshly added monomer (Fig. 4) showing that termination is negligible during the polymerization.

Monomer reactivity ratios in copolymerization

For the determination of the monomer reactivity ratios, a series of copolymerizations with varying monomer feed compositions have been carried out and terminated at low (< 8%) conversion. The composition of copolymers, as a function of comonomer feed ratio, was acquired from their ^{1}H NMR spectra. The results were used to determine the monomer reactivity ratios by the Kelen-Tüdös method [17]. Fig. 5 shows the Kelen-Tüdös plot where the reactivity ratios r_1 and r_2 for the monomer pair M_1 (IBVE) and M_2 (MVE) can be determined by the linear equation

$$\eta = [r_1 + (r_2 / \alpha)]\xi - (r_2 / \alpha) \qquad (1)$$

where $\eta = G / (\alpha + F)$ and $\xi = F / (\alpha + F)$ (2)

with $\alpha = (F_{\min} \cdot F_{\max})^{1/2}$ (3)

and where $G = x(y - 1) / y$ and $F = x^2 / y$ (4)

with $x = [M_1] / [M_2]$ and $y = d[M_1] / d[M_2]$ (5)

The reactivity parameters obtained are r_{IBVE} = 1.08 and r_{MVE} = 0.43. The copolymerization curve, obtained with these values, is shown in Fig. 6.

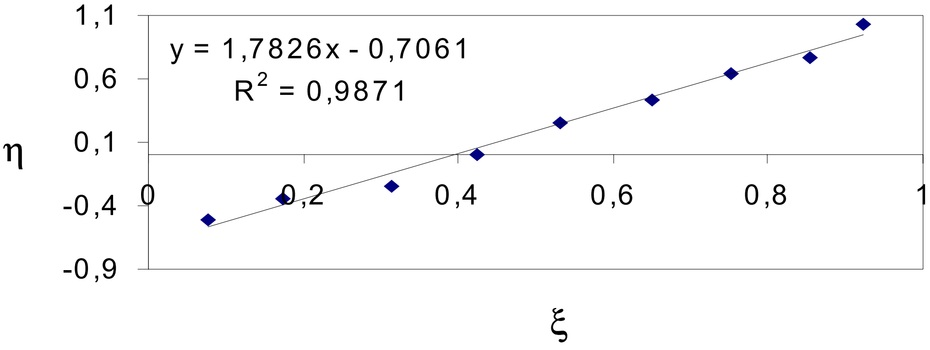


Fig. 5. Determination of reactivity ratios by the Kelen-Tüdös method

Polymers with a MVE unit as active species have a tendency to cross-propagate with IBVE ($k_{22} < k_{21}$), indicating that IBVE is a more reactive monomer than MVE. This can be explained by the larger inductive effect of the isobutyl group in comparison with the methyl group, whereby the electron density in the IBVE vinyl group is higher than in the MVE vinyl group. Polymers with an IBVE unit as active species have no preference for one of the monomers ($k_{11} \cong k_{22}$). This could be due to the presence of sterically hindering substituents on the active species as well as on the monomer in the case of homopropagation with IBVE. This effect would compensate for the difference in electron density of the monomers.

Due to the living character of the copolymerization and taking into account the r_1 and r_2 values, the copolymers, obtained after complete conversion, should show a moderate gradient-type structure.

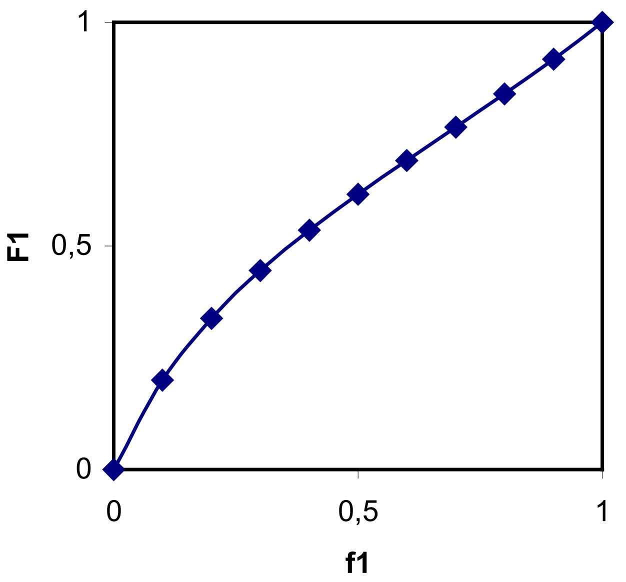


Fig. 6. Plot of the variation of copolymer composition (F_1) with comonomer composition (f_1), where **1** is IBVE. The solid line is the calculated copolymerization curve obtained with $r_{IBVE} = 1.08$ and $r_{MVE} = 0.43$

Properties of the copolymers

All copolymers were sticky, viscous materials at room temperature as was expected from the glass transition temperatures of the homopolymers (T_g of PMVE: -34°C and T_g of PIBVE: -19°C).

Tab. 2. Solubilities of poly(IBVE-*co*-MVE) (at 20°C) (+: soluble, 0: insoluble, ±: partly soluble)

Solvents	PMVE [a]	PIBVE [b]	Poly(IBVE-*co*-MVE) [c]
Water	+	0	0
Methanol	+	0	+
Ethanol	+	±	+
CH_2Cl_2	+	+	+
Cyclohexane	0	+	+
Diethyl ether	±	+	+
Acetone	+	+	+

[a] M_n (PMVE) = 3 000 g/mol. [b] M_n (PIBVE) = 7 000 g/mol. [c] Poly(IBVE-*co*-MVE) with mole ratio 32/68 (M_n = 4 990 g/mol) and 70/30 (M_n = 6 970 g/mol).

Tab. 2 shows some solubility properties of the homopolymers and copolymers. PIBVE is insoluble in polar solvents (water, methanol), PMVE, to the contrary, is soluble in polar solvents. The copolymers are soluble in all organic solvents but are insoluble in water when the weight fraction of IBVE exceeds 10 wt.-%. The LCST behaviour, typical of PMVE, disappears when the copolymer contains more than 10 wt.-% (i.e., 6% mole fraction) of IBVE. This means that the LCST of PMVE of molecular weight 3 000 is already strongly influenced by the presence of a few IBVE units in the PMVE-chain. With 6 mol-% of IBVE (i.e., a polymer consisting of 50 MVE and 3 IBVE units), the cloud point was determined to be 10°C (0.25 wt.-% aqueous solution). With one additional IBVE unit, the polymer becomes insoluble. The strong influence of small fractions of hydrophobic groups on the LCST properties has been reported earlier for PMVE's containing hydrophobic end groups [18].

Experimental part

Materials

Toluene and diethyl ether were distilled over sodium in the presence of traces of benzophenone, as an indicator for the presence of H_2O, just before use. Trimethylsilyl iodide (Aldrich, 97%, 5 ml ampoule) was used without purification. Isobutyl vinyl ether (Acros Organics, stabilized, 99.5%) was distilled over calcium hydride and, just before use, over sodium. Methyl vinyl ether was obtained from BASF company (Ludwigshafen). 1,1-Diethoxyethane (Acros Organics, 99%) and triethylamine (Aldrich, 99.5%) were distilled over CaH_2 just before use. Zinc iodide (Aldrich, 99.99%) was dried in vacuum before use. Methanol was refluxed and distilled over calcium oxide before use.

Copolymerization procedures

A typical copolymerization procedure was as follows: 0.58 ml (0.019 M) of TMSI and 0.24 ml (0.016 M) of DEE were added to 100 ml of dry toluene under an argon atmosphere at -40°C using an equipment described in ref. [15]. After 10 min, 5.0 g of MVE and 11.2 ml of IBVE corresponding to a 50/50 mole ratio (1.67 M, 0.172 mol) was added. IBVE was added through a rubber septum by means of a hypodermal syringe. The gaseous MVE flowed through stainless steel tubing into the reactor where it condensed in the cooled toluene solution. The amount and the mass flow of MVE were measured by a mass flow controller. The reactor was warmed to 0°C and the polymerization was started with the injection of 27 mg of ZnI_2, dissolved in 3 ml of diethyl ether. After 4 h, 10 ml of methanol followed; 1 min later, 2.88 ml (0.204 M) of triethylamine were introduced to terminate the reaction. The reaction mixture was washed with 10% aqueous sodium thiosulfate solution and water, dried over $MgSO_4$, filtered and the filtrate evaporated to dryness under reduced pressure.

Analytical methods

GPC analyses were performed with $CHCl_3$ as eluent with a 60 cm Polymer Laboratories column, porosity 10^3 Å, and calibrated with polystyrene standards. ^1H NMR spectra were recorded on a Bruker AC360 FT instrument.

Conclusions

The copolymerization of IBVE and MVE, initiated by the system DEE/TMSI/ZnI_2, at 0°C in toluene, is living, just as the homopolymerization of these vinyl ethers.

The copolymerization monomer reactivity ratios, obtained by the Kelen-Tüdös method, are $r_{IBVE} = 1.08$ and $r_{MVE} = 0.43$ and therefore, the copolymers obtained at high conversions have a (slightly) gradient structure.

Poly(IBVE-*co*-MVE) is water-soluble only if the IBVE content is 10 wt.-% or lower.

The LCST behaviour of a PMVE polymer is strongly influenced by introducing a small fraction of IBVE. The cloud point temperature of a 0.25% solution of a copolymer containing 6 mol-% of IBVE was 10°C as compared to 37°C for the pure PMVE.

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