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### ETHYLENE OXIDE EFFECT ON THE POLYMERIZATION OF *TERT*-BUTYLACRILATE AND SYNTHESIS OF POLYETHER-POLYESTER TYPE BLOCK-COPOLYMERS

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## ETHYLENE OXIDE EFFECT ON THE POLYMERIZATION OF *TERT*-BUTYLACRYLATE AND SYNTHESIS OF POLYETHER-POLYESTER TYPE BLOCK-COPOLYMERS

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### ABSTRACT

*Tert*-butylacrylate was polymerized by potassium *tert*-butoxide in THF and toluene in the presence of 10% (by volume) of ethylene oxide. Polymers with good yields and reasonably narrow MWD ( $M_w/M_n \sim 2$ ) were obtained. Microtacticity of the polymers is strongly solvent-dependent, the content of isotactic triads being ~70% in toluene and ~40% in THF.

Upon using ethylene oxide as part of the solvent, diblock-copolymers of polyethylene oxide with poly-*tert*-butylacrylate with controlled molecular weight characteristics of the polyethylene oxide block were synthesized. The possibility of diethylvinylphosphonate polymerization on the living chain ends of poly-*tert*-butylacrylate was checked. At the 10% content of ethylene oxide in the reaction medium, diblock-copolymers of poly-*tert*-butylacrylate and polydiethylvinylphosphonate were obtained and their compositions were determined.

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Triblock-copolymers polyethylene oxide-poly-*tert*-butylacrylate-polydiethylvinylphosphonate with low polymerization degree of the second and the third blocks were prepared.

*Key Words:* Anionic polymerization; Ethylene oxide; *tert*-Butylacrylate; Diethylvinylphosphonate; Di- and tri- block-copolymers.

## INTRODUCTION

Polymer materials based on acrylates and methacrylates are widely used in different technical applications (e.g., as transparent plastics, textile and optic fibers, as well as elastomers, including highly porous rubber). Industrial production of these materials is continuously growing and improved synthetic approaches are being developed. Therefore, the study of fundamentals of anionic polymerization, especially that of acrylates and methacrylates is of great importance.

In the recent past, such studies were concentrated on the search for new initiating systems which could provide the synthesis of polymers with predictable parameters of molecular weight and molecular weight distribution. An analysis of experimental data published until now shows that a tremendous success in the development of highly effective initiating system by modifications of lithium organic compounds with different reagents has been achieved [1–8].

In contrast, during the last decade, investigations of initiating systems derived from alcoholates of alkali metals have been rather scarce [9–14]. In the cited literature, only using potassium-*tert*-butoxide (t-BuOK) for polymerization of methacrylates is documented.

In the present paper, the possibility of utilization strong solvating properties of ethylene oxide (EO) to increase the reactivity of t-BuOK in polymerization of *tert*-butylacrylate (tBA) in toluene or THF was investigated. Solvating effect of EO in the synthesis of diblock-copolymers of polyethylene oxide (PEO) with poly-*tert*-butylacrylate (PtBA) and triblock-copolymers of PEO, PtBA and polydiethylvinylphosphonate (PDEVVP) was also studied.

## EXPERIMENTAL

### Reagents

t-BuOK was synthesized according to the well-known method [15]. Traces of *tert*-butanol (t-BuOH) were removed by multiple solvent (toluene) replacement. In all polymerization experiments, the initiator was used in the form of its THF-solution.

Purification of and water traces removal from ethylene oxide (EO, Fa. Merck) was performed in a all-glass vacuum apparatus ( $10^{-3}$  mbar), first with  $\text{CaH}_2$  and then with concentrated n-BuLi (Fa. Fluka).

Consequently, *tert*-Butylacrylate, with  $\text{Al}_2\text{O}_3$  and  $\text{CaH}_2$ , was purified under vacuum, then in vacuum (60 mm Hg) distilled and, finally, was dried over  $\text{CaH}_2$  and recondensed.

Diethylvinylphosphonate (DEVP) was synthesized by known methods [16]. DEVP was dried by boiling with  $\text{CaH}_2$  and subsequently, distilled in vacuum (60 mm Hg). Such a procedure was repeated three times. Finally, gaseous impurities were removed from DEVP under vacuum ( $10^{-3}$  mbar) in a all-glass vacuum apparatus.

Toluene was purified by a commonly accepted procedure. First, toluene was treated with  $\text{CaH}_2$  and concentrated *n*-BuLi in a all-glass vacuum apparatus. Final purification of the solvent was achieved by its treatment with oligostyryl lithium in a all-glass vacuum apparatus.

THF was in a vacuum all-glass apparatus by K/Na-alloy purified until the "blue" solution is formed. All solutions with non-distillable purified reagents such as DEVP and the initiator (*t*-BuOK), were dosed in high vacuum ( $10^{-6}$  mbar), using the special, so-called "spider" apparatus. Volatile solvents and monomers (EO, tBA) were dosed with a specially so-called "comb" apparatus.

### Polymerization

All polymerizations were carried out in a special all-glass apparatus in high vacuum ( $10^{-6}$  mbar). The homopolymerization of EO was performed in toluene or THF at room temperature (for 72 hours). tBA was homopolymerized by *t*-BuOK in toluene or THF, both in the presence and absence of 10% of EO in the solvent medium. Homopolymers of DEVP, as well as block-copolymers PEO-*b*-PtBA or PEO-*b*-PtBA-*b*-PDEVP, were obtained in a two-chamber reactor [12]. The block-copolymers were synthesized in two or three stages. Initially, the homopolymerization of EO was carried out, followed by the subsequent additions of tBA and DEVP solutions into the reaction mixture at low temperature ( $-50^\circ\text{C}$  to  $-35^\circ\text{C}$ ). Polymerization was terminated by adding the 4:4:1 mixture of ethanol, toluene, and acetic acid. After evaporating the solvent mixture, the residue was repeatedly washed out by hexane and, finally, dried in vacuum.

### Polymer Characterization

Purified polymers were characterized by NMR- spectroscopy and gel permeation chromatography (GPC).  $^1\text{H}$  NMR spectra were recorded on a DRX500 (Bruker) at 500.13 MHz,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR-spectra were obtained using a MSL300 (Bruker) at 75.48 and 121.5 MHz, respectively, in  $\text{CDCl}_3$ -solutions at room temperature. The tacticity was determined by the triad signals of  $\alpha\text{-C}$  in  $^{13}\text{C}$  NMR spectra [17]. GPC-measurements for determining molecular weights and molecular weight distributions were carried out with THF as eluent (flow rate 1 mL/min; temperature of columns  $40^\circ\text{C}$ ; 3 columns, 30 cm each;  $5\mu\text{m}$  Plgel,  $10^2$ ,

$10^3$ ,  $10^4$  Å (Fa. Clausen); Device and detector: Hewlett-Packard 1090 liquid chromatography with DAD and HP RID 1037 Å). Polystyrene standards were used for calibration.

## RESULTS AND DISCUSSION

### Polymerization of *tert*-Butylacrylate in the Presence of Ethylene Oxide

Among acrylic and methacrylic monomers of great industrial significance, methacrylates capable of living anionic polymerization are under the most intensive investigation [18]. The polymerization of acrylates is principally complicated by termination and transfer reactions [5].

Recently, Müller *et al.* have proved the “living” and controllable polymerization of *tert*-butylacrylates by ethyl- $\alpha$ -lithium isobutyrate in the presence of complexes of  $\text{NR}_4^+[\text{Al}_2\text{R}_6\text{X}]^-$  type [7]. This discovery opens up a wide range of possibilities to synthesize block-copolymers from various polyacrylates and polymethacrylates. However, block-copolymers of poly-(ethylene oxide-*b*-acrylate) type are still not obtainable with this initiating system. For the latter block-copolymerization, two conditions are to be met: 1) an initiator with potassium counterion, able to polymerize EO, should be used; 2) potassium alcoholate (“living” polyethylene oxide) should be able to initiate polymerization of acrylate monomers. So far, it was impossible to polymerize acrylates by alcoholates of alkali metals. It is well-known that these alcoholates are ineffective initiators for methacrylates as well. Thus, initiation efficiency ( $f$ ) of methyl methacrylate (MMA) polymerization by *t*-BuOK is only 0.003 and 0.043 in toluene and THF, respectively [12]. Upon the addition of strong electron donors as solvating reagents the initiation efficiency is drastically increased, up to the  $f$ -value of 0.21 in the case of dicyclohexyl-18-crown-6 and 0.61 in the case of 2,2,2-cryptands [9]. Similar effect of EO as the solvent medium on the initiation efficiency of MMA polymerization was observed ( $f=0.7$ ) [12].

In the present paper, solvating properties of EO were utilized for the enhancing initiation efficiency of tBA polymerization by *t*-BuOK in toluene or THF. For comparison, tBA polymerization by *t*-BuOK in both toluene and THF without EO was once attempted. The results obtained show that in the temperature range from  $-78^\circ\text{C}$  to  $-40^\circ\text{C}$  no polymerization occurs in the absence of EO, regardless of both the initiator and tBA concentrations. The results obtained in the presence of 10% (by volume) of EO are presented in Table 1. As seen from the data, the suggested initiating system makes it possible to polymerize tBA up to high monomer conversions. Obtained PtBA samples are characterized by relatively narrow molecular weight distributions,  $M_w/M_n \sim 2$  (Figure 1). The values of polydispersity index known from published data for ethyl- $\alpha$ -lithium isobutyrate as the initiator are  $M_w/M_n=60$  in toluene [6] and  $M_w/M_n=7.9$  in THF [5].

In the case of EO addition into the reaction mixture, the initiation efficiency  $f = M_n^{\text{theor.}}/M_n > 1$  (Table 1). For polymerization of acrylates by complex initiating

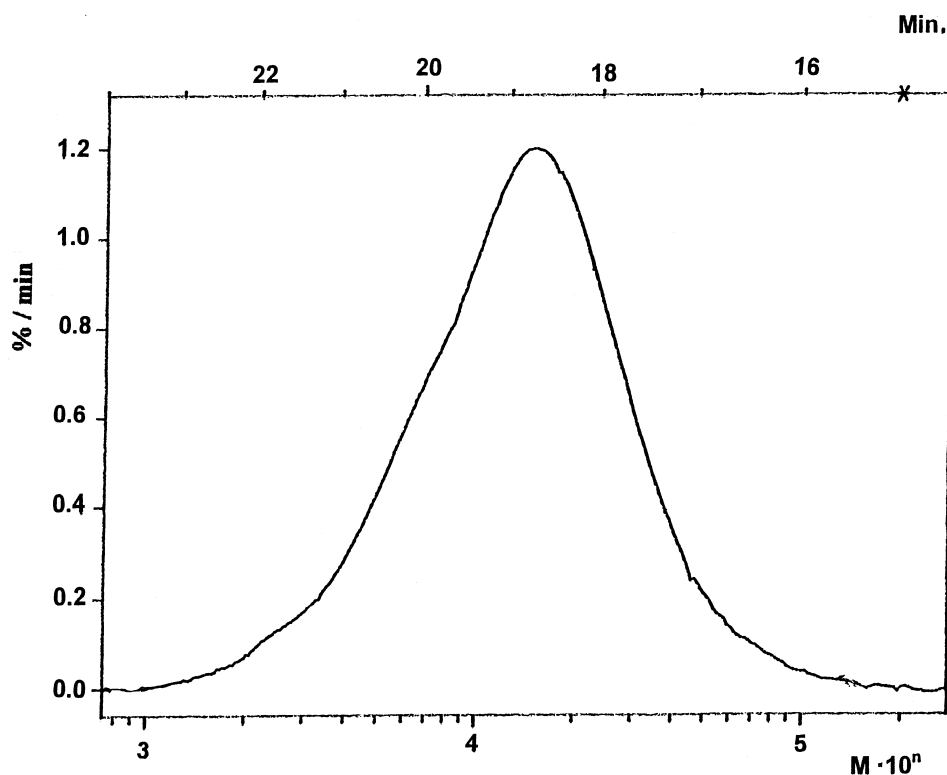


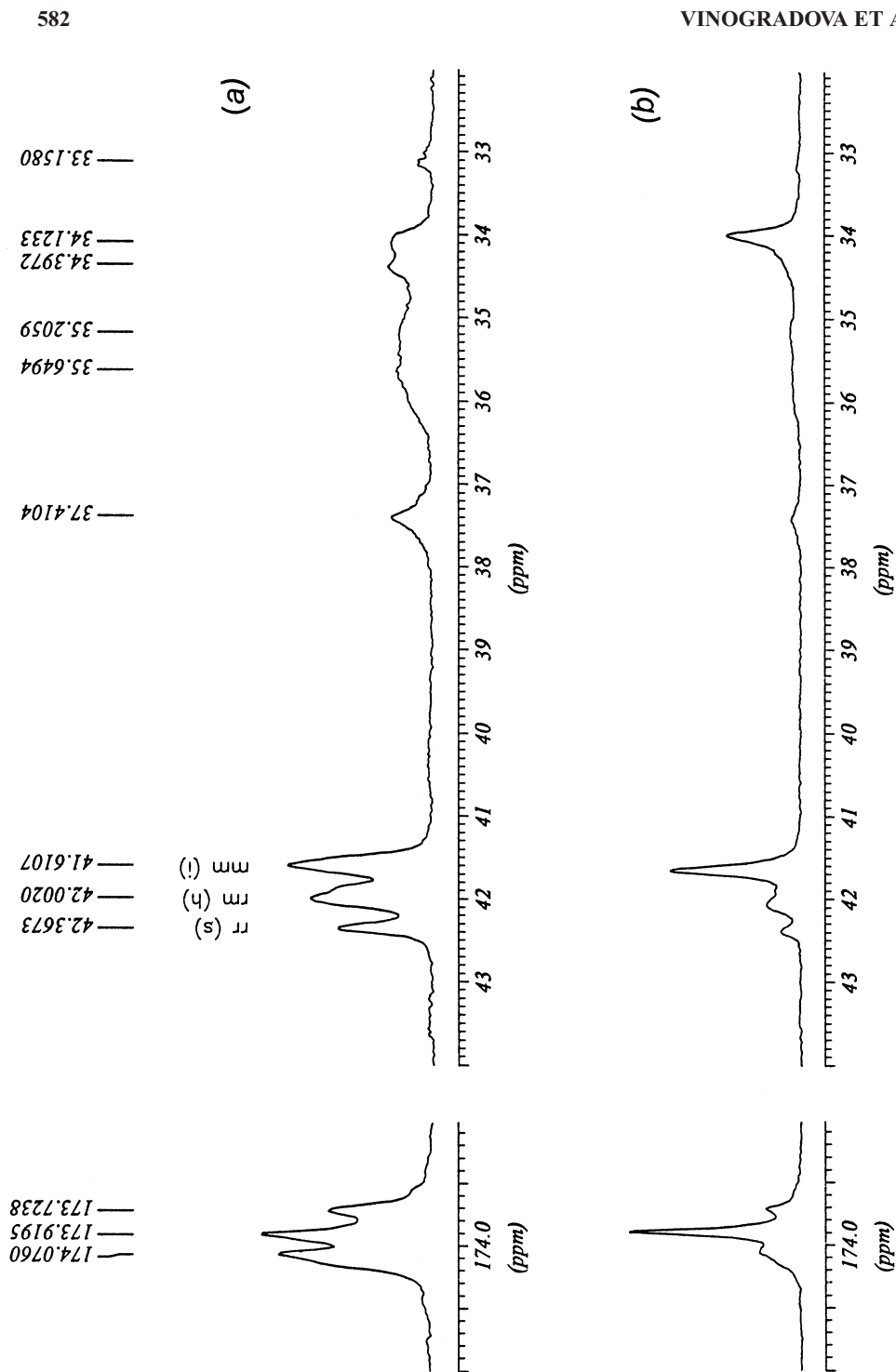
Figure 1. GPC-curve for homo-poly-*tert*-butylacrylate (Table 1, run 2).

systems based on lithium organic compounds, the  $f$ -values  $>1$  were also found [19, 20]. It means that during the polymerization, termination and chain transfer to monomer are possible as side reactions.

The polymers obtained in different solvents differ by their tacticities, as follows from their  $^{13}\text{C}$  NMR spectra (Figure 2). The polymers synthesized in toluene are highly isotactic ( $\sim 70\%$  *mm*, Table 2), while those obtained in THF have a lower content of isotactic triads (Table 2).

Table 1. Homopolymerization of *tert*-Butylacrylates in the Presence of Ethylene Oxide (10% with Respect to Total Reaction Volume). Initiator – *t*-BuOK

N	Solvent	$\vartheta$ [°C]	$t$ [min]	tBA [mol/l]	t-BuOK [mol/l] $\cdot 10^3$	Yield [%]	MW (theor.)	$M_n$	$M_w/M_n$	$f$
1	Toluene	-78	90	1.03	3.83	87.0	29900	18900	1.77	1.58
2	Toluene	-35	60	0.85	5.71	99.2	18900	9900	1.76	1.90
3	THF	-50	4	1.55	5.06	96.6	37900	9800	2.36	3.87
4	THF	-40	5	0.66	4.15	99.0	20100	8400	2.05	2.30



**Figure 2.**  $^{13}\text{C}$  NMR spectra of homo-poly-*tert*-butylacrylate synthesized in THF (a) and toluene (b).

**Table 2.** Poly-*tert*-butylacrylate Tacticity Dependence on the Solvent

N	Solvent	$\vartheta$ [°C]	Tacticity, %		
			<i>mm</i>	<i>mr</i>	<i>rr</i>
1	Toluene	-78	70.0	23.0	7.0
2	Toluene	-35	67.5	24.2	8.3
3	THF	-50	47.3	38.6	14.1
4	THF	-40	41.6	41.0	17.4

### Initiating System

The obtained result that, in the temperature range from  $-78^{\circ}\text{C}$  to  $-35^{\circ}\text{C}$ , tBA is polymerized by t-BuOK in the presence of 10% (by volume) of EO, poses a question, "How do t-BuOK and EO interact at these conditions to form an efficient initiating system". To try to answer this question, the reaction between t-BuOK and EO in THF at  $-40^{\circ}\text{C}$  for 30 minutes was attempted and then terminated by water. After recondensation in high vacuum, volatile products derived from the reaction mixture were studied by GC-MS. Besides the initial substances, *tert*-butanol as hydrolyzed product of t-BuOK was identified but no adducts of t-BuOK and EO (e.g., 2-*tert*-butoxyethanol) were detected. *tert*-Butanol was in an equimolar amount with respect to the consumed t-BuOK found.

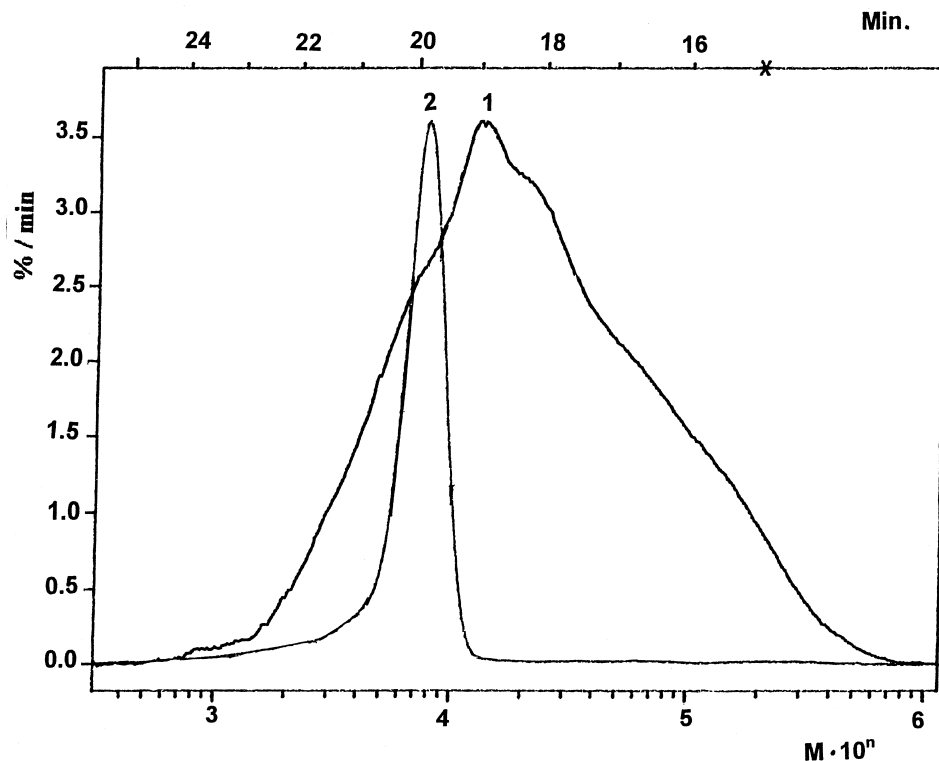
It is well-known that t-BuOK forms very stable associates. The association degree is independent on temperature and concentration within a wide range, while a remarkable dependence on the dielectric constant of the solvent was observed [21]. The possible explanation of EO effect is as follows. Deaggregation influence of EO results in the shift of the t-BuOK aggregation equilibrium from aggregated towards monomeric forms of t-BuOK. Simultaneously, EO solvates potassium cations, thus enhancing the reactivity of CO-K bonds. From the above presented considerations, it seems to be probable that, during the polymerization, EO acts only as solvating agent (dielectric constant of EO at  $-30^{\circ}\text{C}$  is  $\epsilon = 16.1$  [22]), as no specific reactions proceed.

### Synthesis of Polyethylene Oxide–Poly-*tert*-butylacrylate Diblock-Copolymers

The above described effect of EO was utilized for the synthesis of diblock-copolymers from PEO and PtBA. Block-copolymers of polyether-polyester type are of great practical importance. By the hydrolysis of ester groups of these block-copolymers ionogenic water-soluble products can be obtained. In the literature, di- and triblock-copolymers of PEO with polymethylmethacrylate (PMMA) and PEO with poly-*tert*-butylmethacrylate (PtBMA) have been described [23–26]. However, no diblock-copolymers from PEO and acrylate blocks are reported so far.



At the chosen experimental conditions of block-copolymerization, there is a possibility to control the first stage, i.e., polymerization of EO. EO was quantitatively polymerized by t-BuOK. The obtained polymers are characterized by a narrow molecular weight distribution ( $M_w/M_n \sim 1.1$ , see Figure 3). The second stage of the block-copolymer synthesis was complicated due to high viscosity and crystallization at low temperatures. Therefore, the polymerization of tBA should be performed at heterogeneous conditions. At the molecular weights of PEO of ca. 60000, PEO solutions at  $-40^\circ\text{C}$  form completely crystallized solid phase. For this reason, it is impossible to stir the mixture to provide an efficient mixing of the reactants. In this case, no block-copolymer formation was observed from the  $^1\text{H}$  NMR data (Table 3, run 3). At low molecular weights of PEO (up to 20000, Table 3) the formation of block-copolymers is of higher probability. As follows from the data of Table 3, the second monomer is polymerized on PEO "living" chain ends with high yield. The diblock-copolymers were separated in water into two fractions (water-soluble and water-insoluble). According to the  $^1\text{H}$  NMR data, the water-soluble fraction contains also hydrophobic PtBA (Table 3). These results can be explained by the formation of short second blocks. Water-solubility of this fraction is, thus, due to water-solubility of PEO-blocks. It is rather probable that



**Figure 3.** GPC-curves for diblock-copolymers PEO-PtBA (1) and PEO-prepolymers (2) (Table 3, run 1).

**Table 3.** Synthesis of the Diblock-Copolymers from Polyethylene Oxide and Poly-*tert*-butylacrylate

N	Synthesis of the I. Block (20°C, 72h.)		Synthesis of the II. Block in presence of ~10% EO				Yield of the Copolymers			Composition PEO : PBA		MW <sub>1</sub> :MW <sub>2</sub> (theor.)
	Solvent	EO [mol/l]	t-BuOK [mol/l] · 10 <sup>3</sup>	ϑ [°C]	t [min]	tBA [mol/l]	[ <sup>a</sup> [mol/l] · 10 <sup>3</sup>	Fraction	Part of Fraction	Mole Relation [%]	( <sup>1</sup> H NMR)	
1	Toluene	1.90	7.1	-40	60	1.30	3.5	water-soluble	0.06	98:2	12400:48400	
2	THF	3.04	6.2	-40	30	1.96	2.4	water-insoluble	0.94	33:67	21600:75800	
3	THF	6.08	5.2	0	15	0.3	5.3	water-insoluble	0.84	31:69	57400	

<sup>a</sup>Active center concentration.<sup>b</sup>Homopolymer PEO.

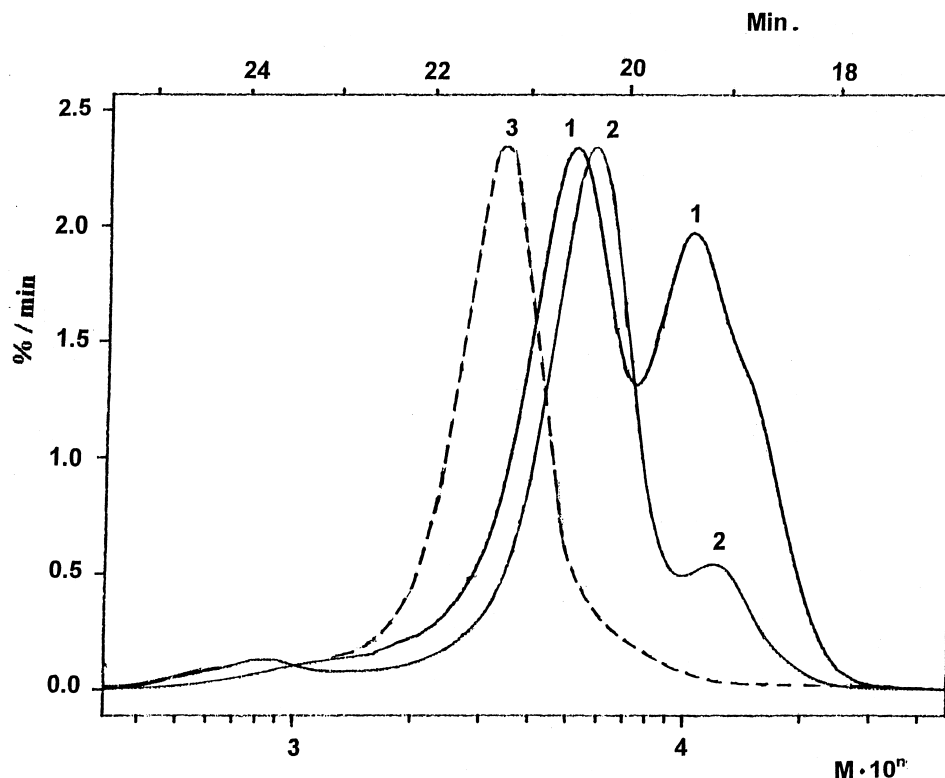
water-soluble diblock-fractions contain also a certain amount of homo-PEO. The data presented in Table 3 show that the block-copolymers have relatively broad molecular weight distributions. This may be related to the specific features of the second monomer polymerization. GPC-curves of the block-copolymers show a considerable amount of a low molecular weight fraction (Figure 3). The molecular weight (MW) of this fraction is lower than MW of PEO-prepolymer (Figure 3). The formation of this fraction could be explained by reactions of chain transfer to the monomer. From the  $^1\text{H}$  NMR data, the molar ratio PEO:PtBA was calculated (the value of the molar ratio was obtained from the integral intensities of proton signals related to the number of protons in the considered groups) for the water-soluble fraction, indicating a high content of PEO-component. In the water-insoluble fraction, the molar amount of PtBA is ca. 2 times higher than that of PEO (see Table 3). These results are in agreement with the calculated compositions (Table 3).

### Synthesis of Polyethylene Oxide–Poly-*tert*-butylacrylate–Polydiethylvinylphosphonate Triblock-Copolymers

To check the applicability of the described initiating system with “EO-effect” for other block-copolymer syntheses, diethylvinylphosphonate (DEVP) was chosen as another monomer. Diblock-copolymers with relatively short second blocks are widely used as emulgators, ion-exchange resins and crystallization promoters. In the case of polydiethylvinylphosphonate (PDEVP), the obtained block-copolymers can additionally be used for surface modification purposes.

To reveal the necessary polymerization conditions, polymerization of DEVP by *t*-BuOK as the initiator was attempted both in the presence and in the absence of EO as part of the solvent medium. An important result is that *t*-BuOK does not polymerize DEVP in the absence of EO. In the presence of EO, highly viscous liquid product was obtained with a good yield.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of the polymer DEVP product show that it consists of a series of short-chain oligomers. The  $^{31}\text{P}$  NMR spectrum shows a great number of peaks in the range from 27 to 34 ppm mostly concentrated around 32 ppm. In the  $^1\text{H}$  NMR spectrum, typical broad signals from the backbone between 1.6 and 2.3 ppm are found. They could be assigned to peaks from multiple low molecular weight oligomers. The intensities of ethyl protons of ester groups correspond to those of backbone protons. It could be thus concluded that the obtained product is of an oligomeric nature due to reactions of chain transfer to the monomer. As the results for the homopolymerization of DEVP demonstrate, the synthesis of block-copolymers of PEO-PDEVP type with the living PEO as macroinitiator is impossible.

It is known from the literature that DEVP is polymerized by anionic initiators containing C-metal bond (e.g., by *n*-BuLi [27]). To synthesize block-copolymers PEO-PtBA-PDEVP, it was necessary to check whether “living” PtBA can initiate the polymerization of DEVP. In the presence of 10% of EO (with respect



**Figure 4.** GPC-curves for the triblock-copolymers PEO-PtBA-PDEV (1) and (2) (Table 4, runs 1 and 2, respectively) and for the PEO-prepolymers (3).

to the total reaction volume), diblock-copolymers from PtBA and PDEV were obtained. The yield for the first block was quantitative. According to the calculation results, the ratio of molecular weights PtBA-PDEV is 16800:1400. The polymerization yield for the second block is ~11%. These results are in a good agreement with the  $^1\text{H}$  NMR data (ratio of polymerization degrees is 131:8).

In this work, polymerization of DEV by the block-copolymer PEO-b-PtBA macroinitiator containing C-K end groups was investigated. Triblock-copolymers obtained in this way were characterized by means of  $^1\text{H}$  NMR- and GPC-measurements. Initially, in two parallel runs PEO-blocks with molecular weights of ~4000 were obtained. Figure 4 shows a considerable shift of peak maximal into high molecular weight region compared to the peak maximal of PEO-blocks, thus indicating an increase of the molecular weight of the diblock and confirming block-copolymerization. The difference in contents of high and low molecular weight fractions in the two experimental runs (Figure 4) can be explained by the difference in experimental conditions, mostly in the stirring efficiency. In general, a complicated character of GPC-curves does not allow one to make a final conclusion on the product composition.

**Table 4.** Synthesis of the Triblock-Copolymers from Polyethylene Oxyde, Poly-*tert*-butylacrylate, and Polydiethylvinylphosphonate (Solvent-THF)

N	Synthesis of the I. Block (20 °C, 72h)			Synthesis of the II. Block (−40 °C, 5 min)		Synthesis of the III. Block (−40 °C, 60 min)		Yield of the Triblock Copolymers [%]
	EO [mol/l]	t-BuOK [mol/l] · 10 <sup>2</sup>	PEO MW <sub>theor.</sub>	tBA [mol/l]	I <sup>a</sup> [mol/l] · 10 <sup>2</sup>	DEVP [mol/l]	I <sup>a</sup> [mol/l] · 10 <sup>2</sup>	
1	2.32	2.44	4200	0.34	1.59	0.57	1.36	75
2	1.84	1.93	4200	0.28	1.33	0.28	1.23	57
3	2.92	1.17	10900	0.82	6.45	0.66	5.63	39

<sup>a</sup>Active center concentration.

**Table 5.** The Composition of the Triblock-Copolymers from Polyethylene Oxyde, Poly-*tert*-Butylacrylate and Polydiethylvinylphosphonate, According to the <sup>1</sup>H NMR Data

N of Triblock- Copolymer	Fraction	Part of Fraction	Composition	
			PEO:PtBA:PDEVP (mol percentage)	PEO:PtBA:PDEVP (according to the degree of polymerization)
1	water-soluble	0.94	90.2:4.7:5.1	96:5:5
	water-insoluble	0.06	—	—
2	water-soluble	1.00	92.3:4.4:3.3	95:4:4
	water-insoluble	—	—	—
3	water-soluble	0.90	84.0:14.1:1.9	248:41:6
	water-insoluble	0.10	40.0:57.1:2.9	249:354:19

It follows from the <sup>1</sup>H NMR data, that the polymerization degree of the second and third blocks is remarkably lower than that of PEO-blocks (see Table 4). Complete water-solubility of the obtained product can be explained by domination of PEO-blocks. Opalescence of the triblock solution indicates its colloidal character.

## CONCLUSION

A new initiating system was found with which it is possible to get homo-PtBA, diblock-copolymers of PEO-PtBA type and also triblock-copolymers of PEO-PtBA-PDEVP type, using easily available and inexpensive reagents.

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