

Controlled polymerization of methylmethacrylate and ethylacrylate using *tris*(4,4'-dimethyl-2,2'-bipyridine) copper(II) hexafluorophosphate complexes and aluminium isopropoxide

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Summary

The radical polymerization of methylmethacrylate and ethylacrylate was carried out in the presence of *tris*(4,4'-dimethyl-2,2'-bipyridine) copper(II) hexafluorophosphate complexes and aluminium isopropoxide. The molecular weight of the synthesized polyethylacrylates increased proportionally with conversion, whereas the polymerization of methylmethacrylate revealed a nonlinear behavior. The polydispersities of the molecular weight distributions observed were between 1.09 and 1.34. Poly(styrene-*block*-polymethylmethacrylate) was synthesized by sequential monomer addition.

Introduction

Generally conventional free radical polymerization yields macromolecules with broad molecular weight distributions (1). In the recent years, research on the controlled radical polymerization which overcome this problem has grown enormously. Especially polyacrylates, polymethacrylates and polystyrenes seems to be suitable for this kind of polymerization processes. Different methods were applied to obtain a controlled radical polymerization: One approach utilizes organic compounds that terminate the growing polymer chain reversibly. Especially stable nitroxide radicals as TEMPO (tetramethylpiperidinyloxy radical) (2-4) and triazoliny derivatives (5) are investigated intensively. Another approach includes organometallic compounds as cobalt(II) or ruthenium(II) complexes (6-8). Furthermore, the polymerization of styrenes and acrylates by atom transfer radical polymerization with copper(I) salts was investigated in detail revealing a good control of the obtained molecular weight as well as narrow polydispersities (9-15). However, polymers obtained by copper(I) salts - like copper(I) bromide or copper(I) chloride - in the presence of *N*-heterocyclic compounds suffer in most cases from a rather high content of copper in the resulting polymers and are therefore partly colored.

Recently, we described a new approach using copper(II) bipyridine complexes (in combination with aluminium isopropoxide) for the polymerization of styrene which overcome some of the disadvantages mentioned above (16). The present paper is an extension of this method describing the polymerization of methylmethacrylate and ethylacrylate monomers.

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Experimental

Materials

4,4'-Dimethyl-2,2'-bipyridine (Aldrich, Reilly Tar & Chem. Corp or synthesized using organo-tin derivatives and Stille-type carbon-carbon bond forming reactions, see e.g. (17)) and $\text{Cu}(\text{CH}_3\text{COO})_2 \times \text{H}_2\text{O}$ (Aldrich) was used as received. Styrene (Fluka), methylmethacrylate (Fluka) and ethylacrylate (BASF AG) were distilled under reduced pressure after destabilizing by passing through an alumina column (Alumina B, ICN). (1-Bromoethyl)benzene (Aldrich), aluminium isopropoxide (Aldrich), 1,4-benzoquinone (Fluka) and acetonitrile (HPLC grade, Fluka) were used as received.

Instruments

Gel permeation chromatography (GPC) analysis was performed on a Waters Liquid Chromatograph system using Shodex GPC K-802S columns, Waters Differential Refractometer 410 and Waters UV Absorption Detector 486 with chloroform as eluent. Calibration was conducted with polystyrene standards.

Synthesis of $[\text{Cu}(\text{II}) (4,4'\text{-dimethyl-2,2'\text{-bipyridine})_3](\text{PF}_6)_2$ (**1**):

4,4'-Dimethyl-2,2'-bipyridine was suspended in $\text{MeOH}/\text{H}_2\text{O}$ (1:1) under nitrogen. A solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \times \text{H}_2\text{O}$ in H_2O was added and the blue colored solution was heated to reflux for 6 h. After addition of an excess of a saturated solution of NH_4PF_6 in methanol a blue solid precipitated immediately. The solid was filtered off, washed with MeOH , H_2O and diethylether, dissolved in acetone and precipitated in diethylether. After filtration the solid was dissolved in a small amount of acetone. By slow diffusion of diethylether into the solution blue crystals of (**1**) (93%) were obtained. UV/VIS (CH_3CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/(\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$) = 285 (32 70). $\text{C}_{36}\text{H}_{36}\text{N}_6\text{CuP}_2\text{F}_{12} \times 2 \text{H}_2\text{O}$ (942.2): Calc. C 45.98, N 8.92, H 4.28. Found C 45.97, N 8.8 1, H 4.21.

Polymerization

A typical procedure was as follows: $[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$ (49.0 mg, 0.24 mmol) and methylmethacrylate (4.21 g, 42 mmol) were added to a solution of (**1**) (54.4 mg, 0.06 mmol) in CH_3CN (0.7 mL) under argon. After addition of (1-bromoethyl)benzene (22.2 mg, 0.121 mmol) the reaction mixture was degassed by three freeze/pump cycles. Then the mixture was heated to 75°C (oil bath) and kept at this temperature during polymerization. Samples (0.1 mL) were taken and quenched with 1,4-benzoquinone in CH_2Cl_2 (2 mL, 27 g/L, 0.25 mol/L) in distinct time intervals. The polymer samples were precipitated in methanol and dried *in vacuo* at 50°C . The conversion was determined gravimetrically.

Results and discussion

The main focus of this work is the design of new effective systems for the controlled radical polymerization of acrylates and methacrylates. Recently, we have demonstrated that the polymerization of styrene with (1-bromoethyl)benzene as initiator in the presence of 4,4'-dimethyl-2,2'-bipyridine copper(II) hexafluorophosphate complexes (**1**) (Figure 1)

and aluminium isopropoxide results in polymers with defined molecular weights and small polydispersities. With the present work we extend the application of this method to methylmethacrylate and ethylacrylate.

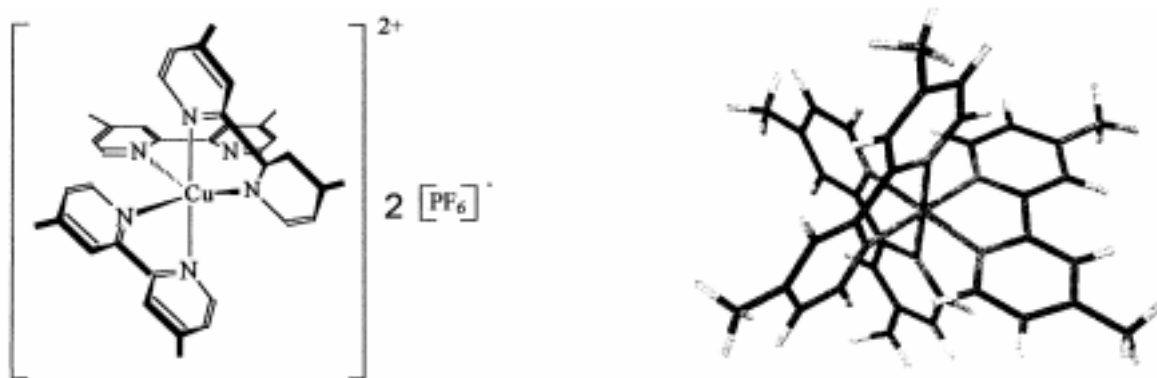
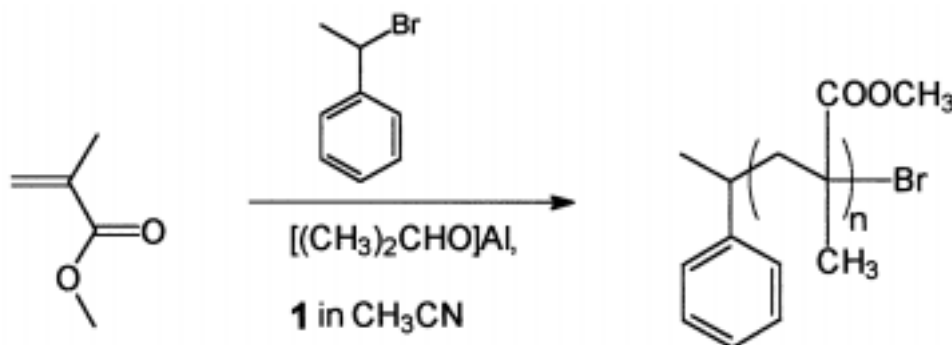


Figure 1: Schematic representation (left) and wireframe model (right) of $[(\text{Cu}(\text{II})(4,4'$ -dimethyl-2,2'-bipyridine) $_3](\text{PF}_6)_2$ (**1**).

Complex **1** was synthesized starting from 4,4'-dimethyl-2,2'-bipyridine in 93% yield. This complex (**1**) was then utilized in the polymerization of methylmethacrylate and ethylacrylate (Scheme 1).



Scheme 1: Polymerization of methylmethacrylate with complex (**1**).

Monomer and aluminium isopropoxide were added to a solution of the complex in acetonitrile (1:700 complex to monomer ratio). After addition of (1-bromoethyl)benzene as initiator the reaction mixture was heated to 75°C. Samples were taken at different times and quenched with 1,4-benzoquinone. The role of the aluminium isopropoxide in the polymerization process is yet not clear but we assume that it acts as a Lewis acid lowering the dissociation energy of the carbon halogen bond in the initiator and the dormant polymeric chain (see also similar results for the polymerization of methylmethacrylate with $\text{RuCl}_2(\text{PPh}_3)_3$ systems (18)). However, recent results indicate that the aluminium isopropoxide also interacts with the used copper(II) complexes in order to reduce copper(II) to copper(I). In that case the polymerization mechanism could follow the proposed ATRP pathway. Further detailed investigation in this direction are currently in progress.

Figure 2 shows the dependence of conversion of methylmethacrylate and ethylacrylate in comparison to styrene. For both methylmethacrylate and ethylacrylate a higher polymerization rate can be observed than for styrene. After 20 h one observed a conversion of 38% for styrene, 58% for methylmethacrylate and 85% for ethylacrylate.

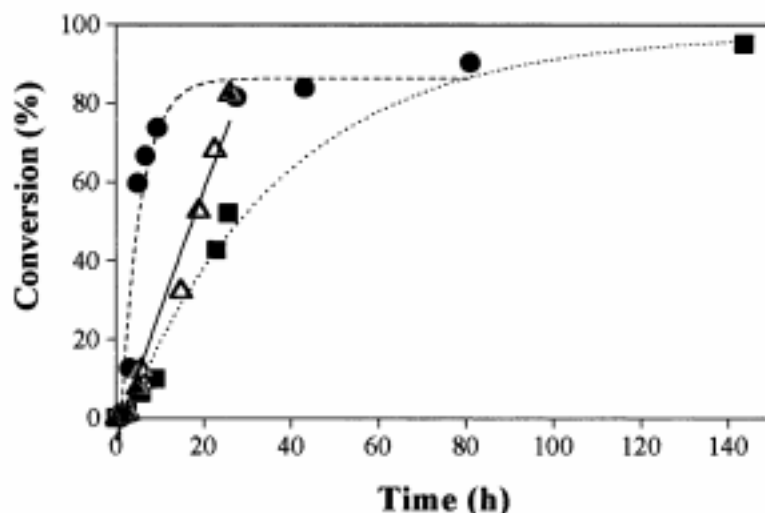


Figure 2: Dependence of monomer conversion as function of time in the polymerization of methylmethacrylate (Δ), ethylacrylate (λ) and styrene (+) (16) at 75°C using (1) ($[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$: 0.24 mmol; monomer: 42 mmol; ratio (1):(1-bromoethyl)benzene = 1:2; ratio 1:monomer = 1:700).

The molecular weight obtained during the polymerization increased linearly with conversion for styrene and ethylacrylate, meanwhile the polymerization of methylmethacrylate showed a completely different characteristics. In the last case the molecular weight increased sharply up to 10% conversion - after reaching this level the $M_n = f(\text{conversion})$ relation became more and more flat. The deviation of the $M_n = f(\text{conversion})$ for polyethylacrylate from the predicted $M_{n, \text{theor.}} ([M]/[I] \times \text{conv.} \times M_{\text{monomer}} + \text{head and end group})$ is probably due to the unsuitable calibration of the GPC with polystyrene standards.

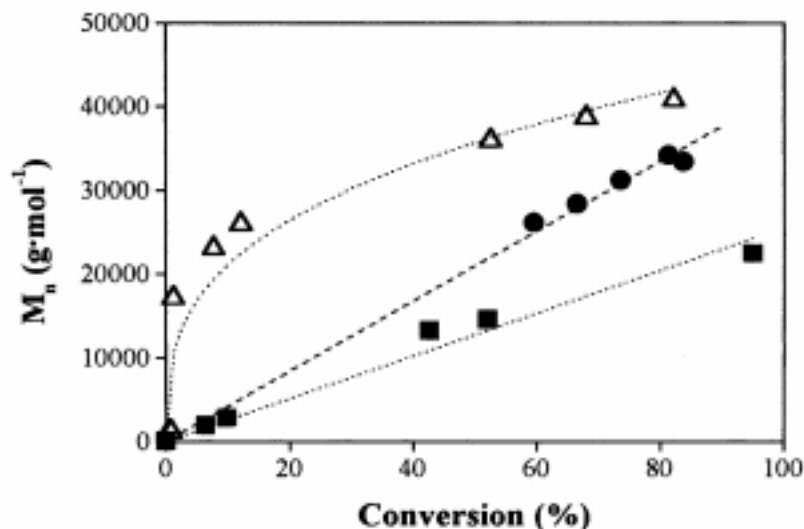


Figure 3: Dependence of the molecular weights as function of monomer conversion in the polymerization of methylmethacrylate (Δ), ethylacrylate (λ) and styrene (+) (16) at 75°C using (1) ($[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$: 0.24 mmol; monomer: 42 mmol; ratio (1):(1-bromoethyl)benzene = 1:2; ratio (1):monomer = 1:700).

Figure 4 compares the molecular weight distributions found in the polymerizations of methylmethacrylate, ethylacrylate and styrene. The best controlled reaction was observed in the polymerization of styrene ($M_w/M_n \approx 1.1$). Polymerization of methylmethacrylate revealed similar results with polydispersities between 1.1 and 1.25.

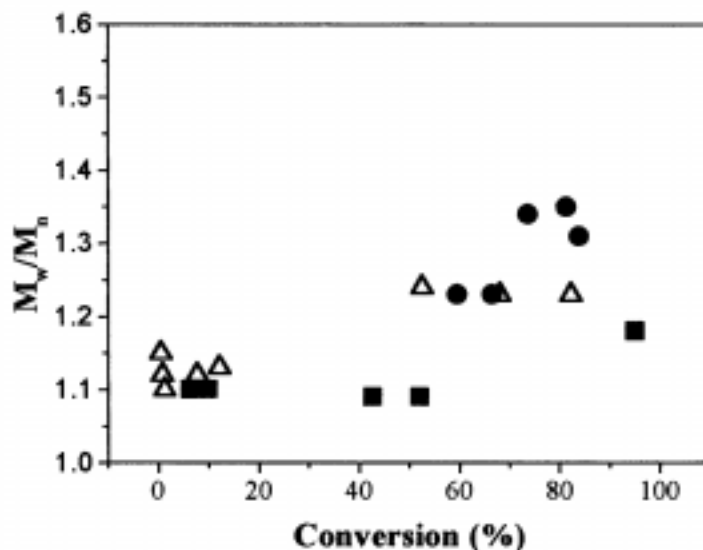


Figure 4. Dependence of polydispersities as function of monomer conversion in the polymerization of methylmethacrylate (Δ), ethylacrylate (\blacktriangle) and styrene (+) (16) at 75°C using (1) ($[(CH_3)_2CHO]_3Al$: 0.24 mmol; monomer: 42 mmol; ratio (1):(1-bromoethyl)benzene = 1:2; ratio (1):monomer = 1:700).

The polydispersities of the resulting polyethylacrylate were broader with values from 1.2 to 1.4. These results are summarized in table 1. In Figure 5 the GPC traces of polymethylmethacrylate and polyethylacrylate samples taken at different conversions are shown.

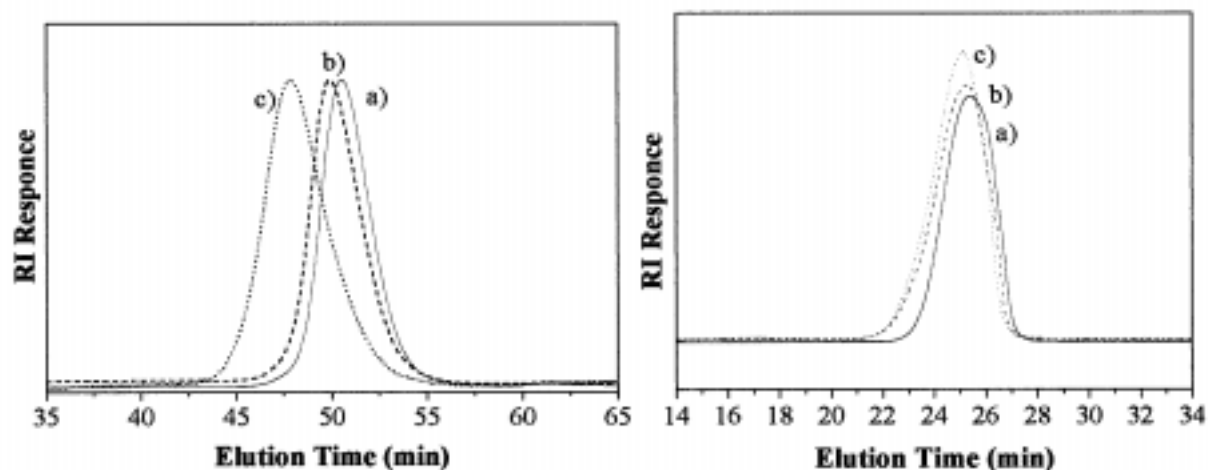


Figure 5: GPC curves (chloroform as eluent) for samples obtained during polymerization of methylmethacrylate (left) and ethylacrylate (right) in the presence of (1) ($[(CH_3)_2CHO]_3Al$: 0.24 mmol; monomer: 42 mmol; ratio (1):(1-bromoethyl)benzene = 1:2; ratio 1:monomer = 1:700): methylmethacrylate (left): (a) 7.8%, (b) 12.2%, (c) 82.2%; ethylacrylate (right): (a) 66.6%, (b) 73.7%, (c) 83.9%.

Table 1: Molecular weight data of different prepared polymers ($[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$: 0.24 mmol; monomer: 42 mmol; ratio (1):(1-bromoethyl)benzene = 1:2; ratio (1):monomer = 1:700).

Monomer	Time (min)	Conversion (%)	$M_n^{a)}$ ($\text{g}\cdot\text{mol}^{-1}$)	M_w/M_n	$M_n^{b)}$ ($\text{g}\cdot\text{mol}^{-1}$)
MMA	20	0.5	1 100	1.15	360
	80	0.8	1 200	1.13	465
	165	1.3	17 000	1.13	640
	295	7.8	23 050	1.12	2 915
	345	12.2	25 900	1.13	4 455
	1135	52.6	35 900	1.24	18 595
	1355	68.1	38 700	1.23	24 020
	1560	82.2	40 800	1.23	28 955
EA	300	59.6	26 100	1.23	21 045
	405	66.6	28 400	1.23	23 495
	570	73.7	31 200	1.34	25 980
	2589	83.9	33 400	1.34	29 550
Styrene	150	1.4	1 000	1.10	695
	345	6.4	1 900	1.10	2 515
	540	9.9	2 800	1.10	3 789
	1380	42.7	13 200	1.09	15 728
	1540	52.1	14 600	1.09	19 149
	8620	95.1	22 400	1.18	34 801

^{a)} values measured by GPC, calibrated with polystyrene standards; ^{b)} theoretical values

Furthermore, first experiments in the direction of polystyrene-polymethylmethacrylate block copolymers were performed. After a nearly complete conversion of styrene the remaining monomer was removed by evaporation and methylmethacrylate was added. 30 min after the addition of methylmethacrylate the formation of a second peak in the GPC chromatograms could be observed by change of the refractive index and by UV absorption detection (Figure 6, curve a). Due to the fact, that polymethylmethacrylate does not absorb in the used wavelength (254 nm), the second peak could be related to a polystyrene-polymethylmethacrylate block copolymer. After 27 h most of the homopolymer was converted to the polystyrene-*block*-polymethylmethacrylate.

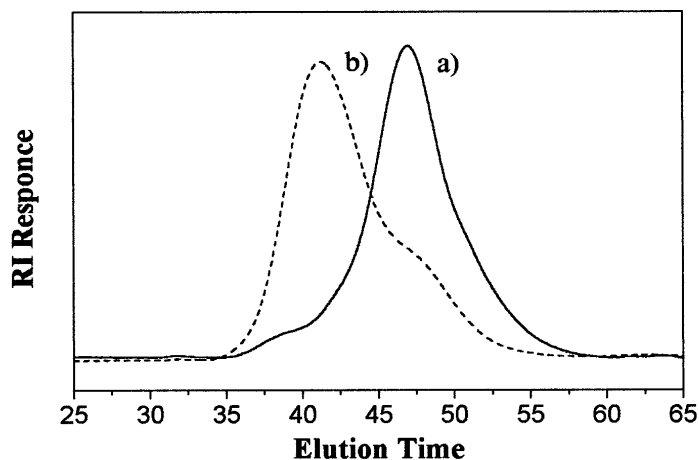


Figure 6: GPC curves (chloroform as eluent) for samples obtained during polymerization of methylmethacrylate with polystyrene in the presence of (1) ($[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$: 0.29 mmol; styrene: 51 mmol; ratio 1:(1-bromoethyl)benzene = 1:2; ratio 1:monomer = 1:700, addition of MMA (51 mmol) after 50 h): (a) GPC trace 0.5 h after addition of methylmethacrylate, (b) GPC trace 27 h after addition of methylmethacrylate.

Conclusions

Tris(4,4'-dimethyl-2,2'-bipyridine) copper(II) hexafluorophosphate complexes in conjunction with aluminium isopropoxide and (1-bromoethyl)benzene is able to polymerize methylmethacrylate and ethylacrylate. It was found, that the polymerization rates depend strongly on the used monomer. In the case of ethylacrylate a good control of the molecular weight via $[M]/[I]$ and conversions is possible, whereas molecular masses of polymethylmethacrylate grow more or less uncontrolled. However, both methylmethacrylate and ethylacrylate polymerized in the presence of *tris*(4,4'-dimethyl-2,2'-bipyridine) copper(II) hexafluorophosphate complexes reveal narrow molecular weight distributions. Furthermore, the formation of a polystyrene-*block*-poly methylmethacrylate was possible. We are working currently on detailed studies about the mechanism of the process.

Acknowledgements

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