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Mechanism of anionic polymerization of (meth)acrylates in the presence of aluminium alkyls

3. MALDI-TOF-MS study on the vinyl ketone formation in the initiation step of methyl methacrylate with *tert*-butyl lithium *

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Summary

Methyl methacrylate was polymerized with *tert*-butyl lithium in the presence of triethylaluminium or triisobutylaluminium at –78°C in toluene. As indicated by GPC and MALDI-TOF mass spectrometry, the polymerization is accompanied by side reactions. The lower oligomers were fractionated by distillation and characterised by NMR, FT-IR, UV and electron impact (EI) mass spectrometry. All these data show that part of the polymer chains are carrying exactly one *tert*-butyl isoprenyl ketone unit. In order to avoid the formation of *tert*-butyl isoprenyl ketone a molar ratio of Al/Li > 2 is necessary.

Introduction

In the polymerization of methyl methacrylate initiated with lithium alkyls it was reported that the initiator, especially n-butyl lithium, attacks both the vinyl and the carbonyl bond of the monomer in the initial step of polymerization[1-6]. The latter reaction results in an alkyl isoprenyl ketone and affects initiator efficiency and control of the molecular weight of the polymer. Additionally, the isoprenyl ketone adds statistically during polymerization, which leads to a "dormant" isoprenyl ketone-terminated chain end. Compared to a methacrylate-terminated chain end, the isoprenyl ketone-terminated chain end is less reactive because of a higher delocalization of negative charge. Consequently, deviations from ideal kinetics and molecular weight distributions have to be taken into account.

It was reported that the polymerization of methyl methacrylate in toluene initiated by *tert*-butyl lithium in the presence of aluminium alkyls was free of side reactions[7-9]. In this publication we present spectroscopic data which indicate that the vinyl ketone formation cannot be suppressed by the addition of aluminium alkyls even at low temperature. The polymers were analyzed by GPC and MALDI-TOF-MS. The lower oligomers were isolated by distillation and the fractions obtained were studied by ^1H, ^{13}C NMR, FT-IR, UV and electron impact (EI) mass spectrometry.

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Experimental

Polymerization: MMA and toluene were purified following established procedures[10,13]. tBuLi (1.7M in pentane, Aldrich) was titrated and used without further purification. $AlEt_3$ and $AlBu^i_3$ (25 wt.-% in toluene, Aldrich) were used as received. All experiments were carried out under slight nitrogen pressure at -78°C. Before adding MMA, the initiator and the aluminium alkyl were mixed at low temperature and stirred for 15-30 min. The reaction was quenched with methanol and the solvent was evaporated. The polymer was dissolved in benzene, filtered and freeze-dried. Isolation of oligomers: After quenching the polymerization reaction with methanol and evaporating the solvent, the lower oligomers were fractionated by vacuum distillation without column. GPC: eluent: THF, detectors: 2x JASCO-UVIDEC 100 III with variable wavelength, Bischoff RI detector 8110; columns: (a) 2x5μ/100Å/60 cm, 1x5μ/500Å/60 cm PL gel, (b) 1x5μ/100Å/60 cm, 1x5μ/linear: 10^2-10^5Å/60 cm PSS gel; calibration was performed using PMMA standards. NMR: ^1H and ^{13}C spectra were recorded with a Bruker AM-400 instrument at room temperature in $CDCl_3$. All chemical shifts were determined with respect to the solvent (^1H: $\delta = 7.24$ ppm, ^{13}C: $\delta = 77.0$ ppm). MALDI-TOF-MS: Spectra were recorded with Kratos Kompact MALDI 3 using a nitrogen laser source ($\lambda = 337$ nm) and 2,5-dihydroxybenzoic acid as matrix. GC-MS: GC: Hewlett Packard 5890 Series II, column: Permabond OV1 (methyl-substituted siloxane, 25m x 0.2 mm, Macherey-Nagel), injector temperature: 150°C, oven temperature: 50-300°C (heating rate: 15°C/min); EI-MS: Trio 2000 (VG Instruments). FT-IR: Spectra were recorded with Mattson 2030 (Galaxy Series FT-IR). UV: Spectra were recorded with Shimadzu UV-240 using $CHCl_3$ as solvent.

Results and discussion

Fig. 1 shows the GPC chromatogram of an oligomeric sample resulting from the reaction of methyl methacrylate with *tert*-butyl lithium in the presence of triethylaluminium at -78°C in toluene ($[tBuLi]/[AlEt_3]/[MMA] = 1/1.6/54$, monomer conversion $x_p = 6.3\%$). Surprisingly, UV absorptions at $\lambda = 260...300$ nm are observed which are incompatible with the expected structure $tBu(MMA)_nH$ ($\lambda_{max} \approx 220$ nm)[11]. Furthermore, a shift in elution volume between the RI and UV signal indicates the existence of two homologous series.

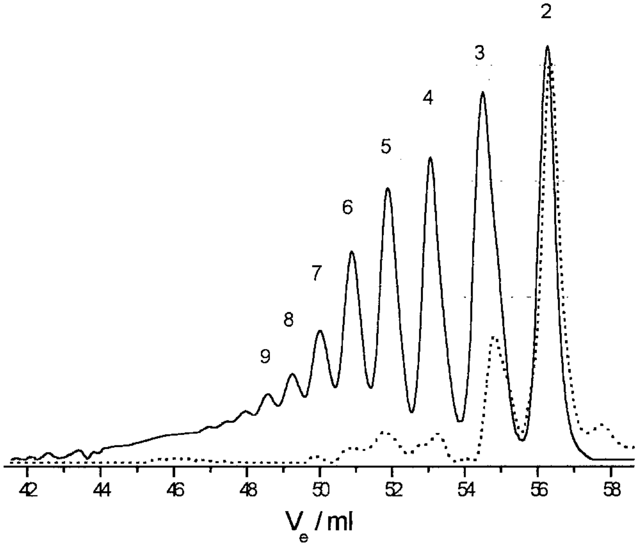


Fig. 1: GPC chromatogram of an MMA oligomer sample formed with $[AlEt_3]/[tBuLi] = 1.6$ at -78°C in toluene. — RI, ···· UV at 300 nm. The numbers correspond to the degree of polymerization, n, of the oligomer $tBu(MMA)_nH$. The unimer is lost in the work-up procedure of the samples[10].

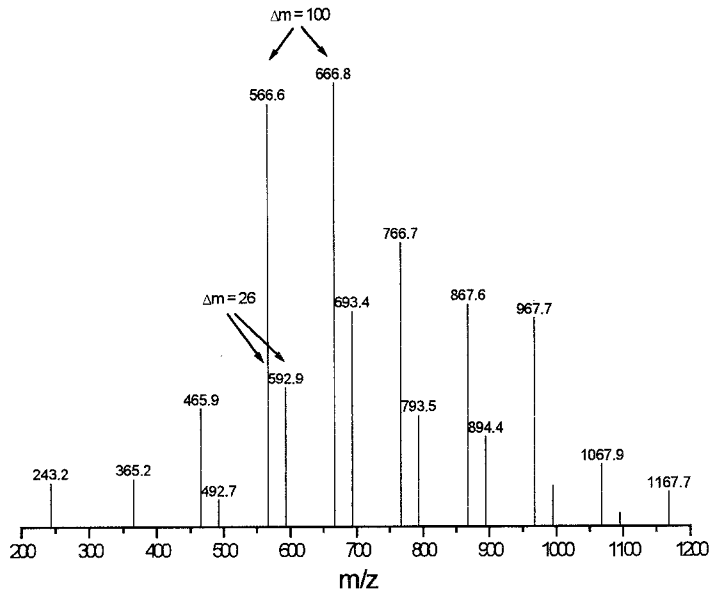
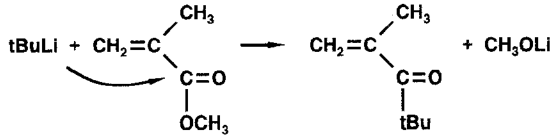


Fig. 2: MALDI-TOF mass spectrum of an MMA oligomer sample formed under reaction conditions described in Fig. 1. The masses correspond to lithium adducts, $[M + Li]^+$. The signal at m/z = 243.2 is presumed to result from fragmentation processes during measurement (cf. Fig. 3).

This chemical heterogeneity is confirmed by the corresponding MALDI-TOF mass spectrum (see Fig. 2). There, two series with a repeat unit of 100 Da (= MMA) but different residual masses of 58 Da and 84 Da ($\Delta m = 26$ Da) are found. A residual mass of 58 Da corresponds to the expected structure $tBu(MMA)_nH$, while 84 Da is compatible with the incorporation of exactly one *tert*-butyl isoprenyl ketone unit (tBVK) into the polymer chain. Backbiting, i.e. formation of cyclic β-ketoesters, can be excluded because this would result in a residual mass of 27 Da which is not found.

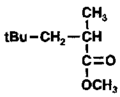
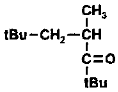
Tert-butyl isoprenyl ketone is supposed to result from the attack of the initiator onto the carbonyl group of the monomer in the initial step of polymerization (Scheme 1):



Scheme 1: Formation of *tert*-butyl isoprenyl ketone (tBVK)

In order to confirm the hypothesis that the second homologous series belongs to a vinyl ketone labelled PMMA, an oligomeric sample (prepared from $[tBuLi]/[AlEt_3]/[MMA]$ = 1/1.1/2.4 at −78°C in toluene) was fractionated by distillation after termination. Two fractions were collected (fraction 1: Bp. = 72-81°C at 50 mbar, fraction 2: Bp. = 65-74°C at 0.02 mbar), each being a mixture of two chemically different components as indicated by GC and GPC. From the NMR, FT-IR and UV spectra (see Tab. 1) and the GC-MS data (see Tab. 1 and Fig. 3), the first fraction could be identified as the hydrolized addition products of methyl methacrylate (tBu-MMA-H, 90 wt.-%) and *tert*-butyl isoprenyl ketone (tBu-tBVK-H, 10 wt.-%), respectively, to *tert*-butyl lithium.

Tab. 1: Spectroscopic and EI-MS data of tBu-MMA-H, and tBu-tBVK-H (fraction 1). ^{1}H NMR, EI-MS: cf. Refs. 5,6.

tBu-MMA-H  $\mathrm{tBu{-}CH_2{-}CH(CH_3){-}C({=}O){-}OCH_3}$	^{1}H, δ/ppm =	0.81 (s, tBu), 1.09 (d, CH_3), 1.79 (dd, CH_2), 2.46 (m, CH), 3.60 (s, OCH_3)
	^{13}C, δ/ppm =	20.2 (CH_3), 29.3 (tBu, CH_3), 30.7 (tBu, C_q), 36.1 (CH), 47.9 (CH_2), 51.4 (OCH_3), 178.2 (C=O)
	FT-IR, $\tilde{\nu}$/cm^{-1} =	1740 (C=O)
	UV, λ_{max}/nm =	—
	EI-MS, m/z =	$[M]^+$ not observed, 159.2 $[M+1]^+$, 143.1 $[M-CH_3]^+$, 127.1 $[M-OCH_3]^+$, 101.1 $[M\text{-}tBu]^+$, 99.0 $[M-COOCH_3]^+$, 57.0 $[tBu]^+$
tBu-tBVK-H  $\mathrm{tBu{-}CH_2{-}CH(CH_3){-}C({=}O){-}tBu}$	^{1}H, δ/ppm =	0.83 (s, tBu), 1.02 (d, CH_3), 1.12 (s, tBu), 1.63 (dd, CH_2), 3.03 (m, CH)
	^{13}C, δ/ppm =	20.8 (CH_3), 27.0, 30.0 (tBu, CH_3), 30.9, 44.6 (tBu, C_q), 36.2 (CH), 47.4 (CH_2), 219.8 (C=O)
	FT-IR, $\tilde{\nu}$/cm^{-1} =	1705 (C=O)
	UV, λ_{max}/nm =	286 (n→π*, broad)
	EI-MS, m/z =	184.2 $[M]^+$, 169.2 $[M-CH_3]^+$, 127.1 $[M\text{-}tBu]^+$, 99.1 $[M\text{-}COtBu]^+$, 56.9 $[tBu]^+$,

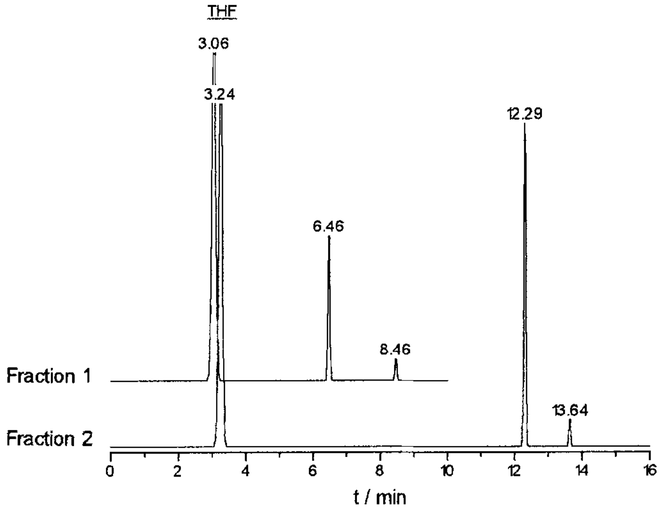
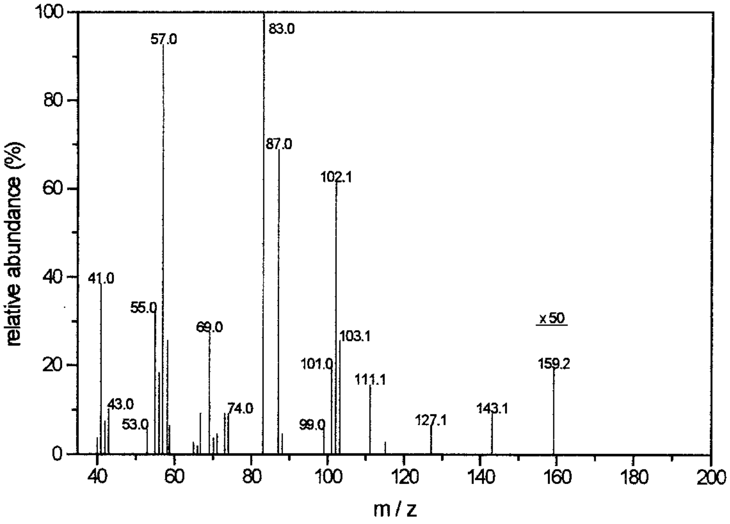


Fig. 3: Gas chromatograms of the two fractions resulting from distillation of the PMMA oligomer prepared with [tBuLi]/[AlEt$_3$]/[MMA] = 1/1.1/2.4 at -78°C in toluene.

GC retention time: 6.46 min
tBu–MMA–H



GC retention time: 8.46 min
tBu–tBVK–H

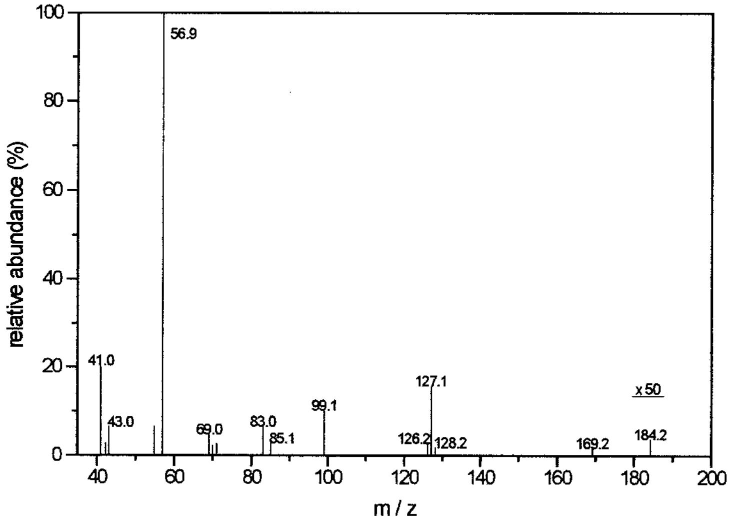
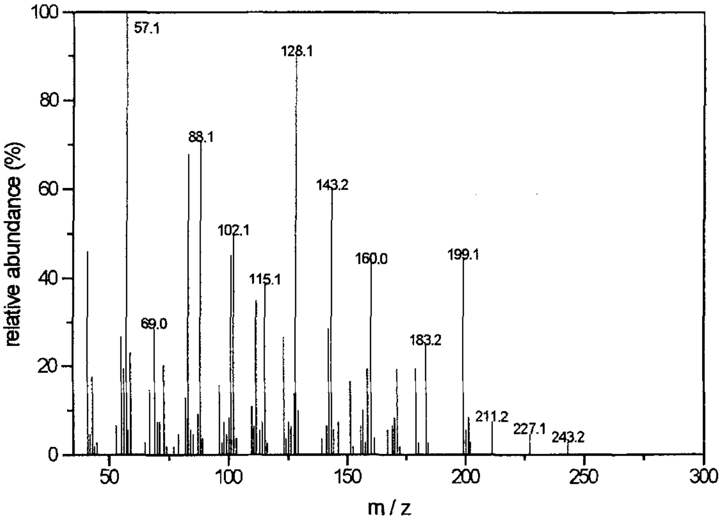


Fig. 3: (continued) EI-MS data of the two components of fraction 1.

GC retention time: 12.29 min
tBu–MMA–MMA–H



GC retention time: 13.64 min
tBu–tBVK–MMA–H / tBu–MMA–tBVK–H

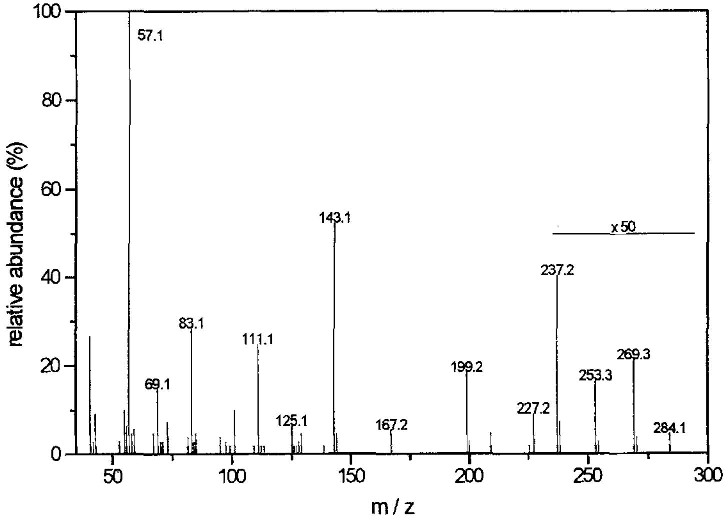
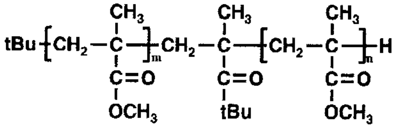


Fig. 3: (continued) EI-MS data of the two components of fraction 2. Similar mass spectra were reported in Refs. 6,12.

The most useful tools in order to demonstrate the existence of *tert*-butyl isoprenyl ketone units in higher oligomers are ^{13}C NMR and FT-IR. The ^{13}C chemical shift of the carbonyl group resulting from the methacrylate unit ($\delta = 178$ ppm) is much more upfield than that of the vinyl ketone unit ($\delta = 219$ ppm). A comparable effect is observed in IR spectra where the absorptions of the carbonyl groups arise at $\tilde{\nu} = 1740$ cm^{-1} and 1705 cm^{-1}, respectively.

The methacrylate dimer, $\mathrm{tBu(MMA)_2H}$, is the major product of the second fraction (> 90 wt.-%; $\delta(^{13}\mathrm{C{=}O}) \approx 177$ ppm; $\tilde{\nu}(\mathrm{C{=}O}) = 1736$ cm^{-1}; $[\mathrm{M}]^+$ not observed, $[\mathrm{M\text{-}CH_3}]^+ = 243.2$). The minor component is regarded to be either tBu–tBVK–MMA–H, tBu–MMA–tBVK–H or a mixture of both ($\delta(^{13}\mathrm{C{=}O}) \approx 178, 219$ ppm; $\tilde{\nu}(\mathrm{C{=}O}) = 1740, 1705$ cm^{-1}; $[\mathrm{M}]^+ = 284.1$). The multiplicity of the carbonyl signals in ^{13}C NMR spectra is presumed to result from different configurational isomers. However, a definite assignment of the signals is not yet possible.

Under usual polymerization conditions ($[\mathrm{tBuLi}]_0 \ll [\mathrm{MMA}]_0$) the concentration of *tert*-butyl isoprenyl ketone is negligible with respect to methyl methacrylate concentration. Therefore, polymer chains with a *tert*-butyl isoprenyl ketone unit directly bound to the *tert*-butyl end group of the polymer are unlikely. Since the addition of *tert*-butyl isoprenyl ketone leads to a "dormant" vinyl ketone-terminated chain end that adds methyl methacrylate after a certain timespan, the polymer chain is supposed to have the following structure[5,6]:



$$\mathrm{tBu}\left[\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\underset{\mathrm{OCH_3}}{\mathrm{C{=}O}}}{\mathrm{C}}}\right]_m\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\underset{\mathrm{tBu}}{\mathrm{C{=}O}}}{\mathrm{C}}}-\left[\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\underset{\mathrm{OCH_3}}{\mathrm{C{=}O}}}{\mathrm{C}}}\right]_n\mathrm{H}$$

If not all of the "dormant" chains add methyl methacrylate, this may lead to a bimodal molecular weight distribution of the polymer (see Fig. 4).

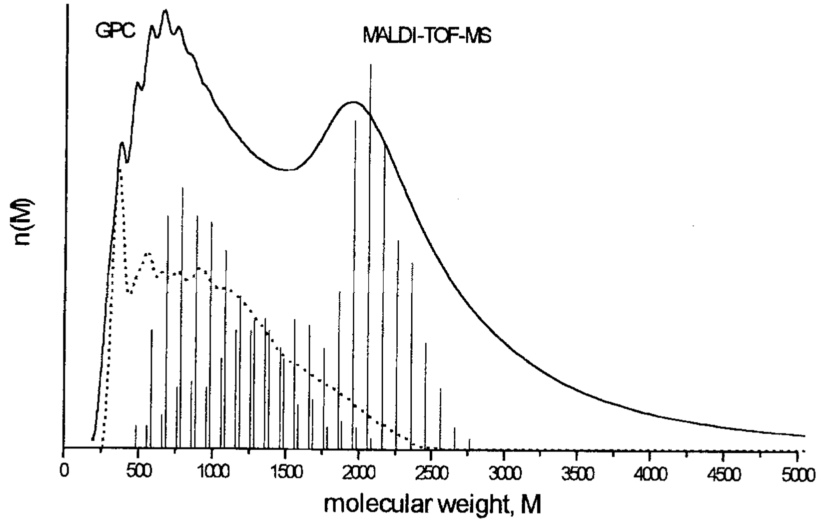


Fig. 4: Frequency distribution n(M) calculated from GPC data (— RI signal divided by M, ··· UV at 300 nm) and MALDI-TOF mass spectrum of a PMMA sample formed with $[\mathrm{tBuLi}]/[\mathrm{AlBu^i_3}]/[\mathrm{MMA}] = 1/3.3/56$ at −78°C in toluene (monomer conversion $x_p = 12.6\%$).

Quantitative analysis of the MALDI-TOF mass spectra shows that the relative amount of *tert*-butyl isoprenyl ketone labelled polymer chains decreases with increasing molar ratio $[AlEt_3]/[tBuLi]$ (= Al/Li). If one uses Al/Li = 1.6, 20% of all polymer chains are labelled with a vinyl ketone unit (see Fig. 2) while Al/Li > 2 leads to almost complete suppression of the vinyl ketone formation. However, even a threefold excess of triisobutylaluminium with respect to initiator leads to 40% of polymer chains carrying a vinyl ketone unit (see Fig. 4) - whether this is an accidental effect or not will be subject of further studies. Vinyl ketone incorporation is also found in poly(methyl methacrylate) formed in anionic polymerization in the presence of triisobutylaluminium at 0°C.[14]

As expected, no signals due to vinyl ketone units in the polymer are observed in MALDI-TOF mass spectra when ethyl α-lithioisobutyrate is used as initiator.

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