Communications to the Editor

Termination Mechanism in the Anionic Copolymerization of Methyl Methacrylate and *tert*-Butyl Acrylate

Owing to the general importance of a large range of poly(alkyl (meth)acrylate)-based products,[1] great interest has been generated during the last few years to the possibility of well-controlled anionic polymerization of (meth)acrylic ester monomers, which are usually polymerized by using kinetically complex radical processes.

A Du Pont research team has already demonstrated that the nucleophile-assisted "group transfer" (GTP) reaction of silylketene acetals may be turned into an efficient living polymerization process for alkyl (meth)acrylates.[2–4] Another strategy followed by us has been to minimize the relative importance of the secondary transfer and termination reactions by surrounding the ion pair of a classical carbanionic growing center with hindering ligands, among which μ-coordinating lithium salts such as LiCl and LiBr were found to be especially practical and efficient.[5–9] This approach has a decisive advantage over GTP because it makes it possible for the block copolymerization of either methyl methacrylate (MMA) or *tert*-butyl acrylate (tBA) with monomers lacking carbonyl-conjugated groups, i.e., styrenes, dienes, heterocyclic monomers, etc. Anionic block copolymerization of MMA and tBA has also been successful with whatever the monomer is first polymerized in the sequential process.[10–12]

In sharp contrast, a hopefully simultaneous copolymerization of these two monomers (statistical or tapered) does not proceed as expected and gives very poor results in terms of conversion and molecular weight distribution. It is the purpose of this preliminary paper to account for that unusual behavior.

Copolymerization reactions (simultaneous or sequential) are typically performed in THF at −78 °C, by using an initiator system (RLi) prepared by reacting *sec*-BuLi with a slight molar excess of α-methylstyrene (α-MS) at room temperature, in the presence of a 10-fold excess of LiCl (with respect to *sec*-BuLi). Rather dilute solutions (ca. 30 vol %) of tBA or mixtures of tBA and MMA in THF are introduced under vigorous stirring, while MMA is added pure. The polymerization time is 15 min for pure monomers and 60 min for tBA–MMA mixtures. The final products are precipitated in acidic methanol–water mixtures (20/80) and dried under vacuum.

Both tBA and MMA homopolymerize in a perfectly controlled manner when exposed to the RLi–LiCl (1/10) initiator system, as indicated in Table I, resulting in practically quantitative yields, initiator efficiencies over 90%, and very narrow MW distributions. Quite unexpectedly, the polymerization of a mixture of these two monomers leads to seemingly erratic results. Comonomer conversion and final molecular weight strongly depend on the composition of the comonomer feed. When tBA content is smaller than ca. 25 mol %, only oligomers of a broad molecular weight distribution are formed within a very poor yield. When the relative amount of tBA is increased, particularly over 50 mol %, both conversion and molecular weight become progressively higher. Whatever the initial composition, the copolymer contains systematically more than 50 mol % tBA units. It is only when that composition is close to 100% that conversion and molecular weight become acceptable again.

On the basis of the experimental observations, it is thus clear that tBA is preferentially copolymerized, in agreement with the well-known higher reactivity of tBA as compared to MMA.[9–13] Furthermore, when a low fraction of MMA units are incorporated in the growing chain, they deeply perturb the living propagation process and eventually stop the otherwise very fast propagation step.

That situation consequently forces us to invoke a specific termination mechanism, which might explain the experimental data. From the many attempts reported in the literature[14–20] to elucidate the termination mechanism in the MMA anionic polymerization, it appears that the experimental conditions may be the determining factor in deciding between three main pathways: termination with monomer, intermolecular termination with ester groups of another polymer chain, and intramolecular termination with the antepenultimate ester group of the same chain (backbiting reaction). Such a backbiting reaction might well explain all of our observations, provided it results from the selective attack of a PtBA anion onto a MMA unit. This is illustrated in Scheme I, which agrees with the proposal of Warzelhan et al. for the MMA polymerization with sodium α-methylstyrene in THF.[21]

The suggested selectivity is supported by the higher sensitivity of the methyl ester group to nucleophilic attack and the rather moderate steric hindrance at the PtBA anion. The alternative reaction, i.e., the attack of a side-chain *tert*-butyl ester group by a PMMA anion, is indeed definitely less probable because of the inductive effect of the *tert*-butyl group and also the steric hindrance in the transition state between the α-methyl group of the PMMA anion and the bulky *tert*-butyl ester group: the latter and probably determining influence is clearly evident from molecular models.

The occurrence of such a termination process is supported by three pieces of experimental evidence. First, a deep violet color appears when a few drops of an aqueous $FeCl_3$ solution is added to an oligomer solution in methanol. This color is characteristic of the iron–enol complex and argues for Scheme I. Second, the NMR spectra of the oligomers display a characteristic enolic proton peak at 12.75 ppm (versus TMS). Third, P(tBA-*b*-MMA) copolymers, resulting from the addition of MMA to living PtBA chains, show no evidence for homo-PtBA formation. When the synthesis is carried out in the opposite way (starting with living PMMA chains to end with P(MMA-*b*-tBA) copolymers), a small amount (ca. 5%) of homo-PMMA is observed, although the overall molecular characteristics of the block copolymer are quite satisfactory ("*f*" values ca. 90%, $\bar{M}_w/\bar{M}_n$ ca. 1.15).[12] These observations support that a MMA unit in the antepenultimate position to a PtBA anion is a favorable situation for the termination reaction to occur. This requirement is never met in the P(tBA-*b*-MMA) copolymers; it is satisfied only two times in the P(MMA-*b*-tBA) copolymers, and it is a common

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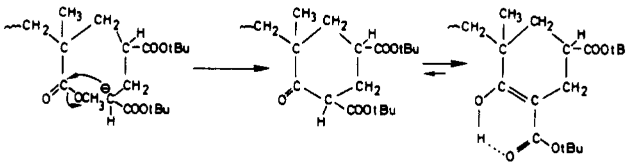
Table I
Anionic Polymerization of MMA–tBA Mixtures in THF at –78 °C[a]

no.	monomers MMA, wt %	 tBA, wt %	$\bar{M}_n$(GPC)[b]	$\bar{M}_w/\bar{M}_n$	tBA in the copolymer (NMR), mol %	yield, %	f[c]
1	100	0	32 600	1.08	0.0	100.0	0.92
2	90	10	2 970	2.2	73.5	6.9	0.85
3	80	20	2 930	2.0	73.7	7.5	0.80
4[d]	80	20	2 910	2.5	87.1	6.8	0.64
5	50	50	23 500	2.1	92.0	17.5	0.78
6	20	80	27 000	2.0	98.2	71.0	0.81
7	10	90	32 000	2.1	99.0	86.0	0.83
8	0	100	31 900	1.07	100.0	100.0	0.94

[a] Initiator was *sec*-BuLi capped with a few units of α-methylstyrene. Polymerization time = 60 min. [b] GPC calibrated with PMMA standards. [c] f; efficiency of the initiator = $\bar{M}_n(\text{calcd})/\bar{M}_n(\text{GPC})$, where $\bar{M}_n(\text{calcd}) = ([M]/[I]_0)(\text{yield}/100)$. [d] In the absence of LiCl, otherwise $[\text{LiCl}]/[\text{I}] = 10$.

Scheme I



situation in the "random" tBA–MMA copolymers when the MMA content of the comonomer feed is significant.

It is worth noting that an equimolar mixture of tBA and tBMA (*tert*-butyl methacrylate) can be copolymerized in a high yield (85%) with formation of a narrow MW distribution ($\bar{M}_w/\bar{M}_n = 1.09$) and a T_g (64 °C) grossly obeying the Fox relationship for a random copolymer. The T_g values of PtBA and PtBMA prepared under the same conditions are 35 and 100 °C, respectively. It was indeed expected that the replacement of a methyl ester (MMA unit) by a *tert*-butyl ester greatly alleviates this kind of termination, for obvious electronic and steric reasons. Finally, another potential termination mechanism, i.e., the bimolecular attack of the MMA monomer by PtBA anions, does not significantly occur since no homo-PtBA was ever observed when preparing P(tBA-*b*-MMA).[12]

The polymerization of tBA–MMA mixtures using various initiators and reaction conditions (solvent, ligand, temperature) will be the subject of forthcoming papers.

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Christian Jacobs, Sunil K. Varshney,
Jean-Paul Hautekeer, Roger Fayt, Robert Jérôme, and
Philippe Teyssié*

Laboratory of Macromolecular Chemistry
and Organic Catalysis, University of Liège
Sart Tilman B6, 4000 Liège, Belgium

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