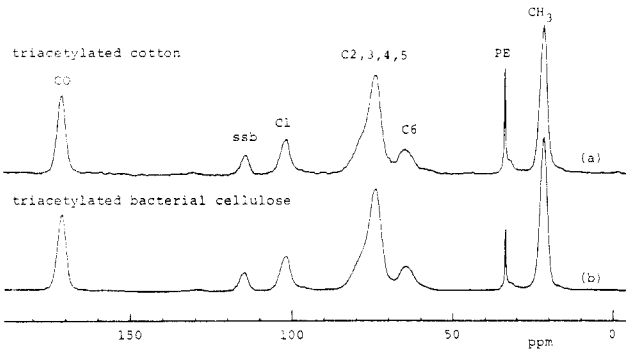

Figure 4. 50-MHz CP/MAS ^{13}C NMR spectra of the triacetylated samples from cotton and bacterial celluloses.

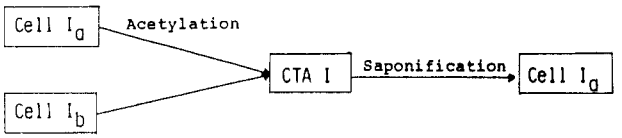

Figure 5. Transformation processes of cellulose crystals by heterogeneous acetylation and saponification.

Marrian and Mann[16] has found the same type of spectrum change in infrared spectroscopy for bacterial and valonia celluloses regenerated from cellulose triacetate, which is in good accord with our results. The same conversion in infrared spectra has also been observed in the case of the regeneration from cellulose III_I, which was prepared by treatment with liquid ammonia at about −50 °C.[16] The examination of the latter process is in progress by CP/MAS ^{13}C NMR spectroscopy.[17]

In order to confirm at which stage the transformation from cellulose I_b to cellulose I_a occurs, we have measured X-ray diffraction patterns and the CP/MAS ^{13}C NMR spectra of triacetylated cotton and bacterial celluloses in the dry state. From X-ray analysis it was difficult to distinguish between the two acetylated samples, and both samples were assigned to cellulose triacetate I (CTA I).[19] Moreover, as shown in Figure 4, the CP/MAS ^{13}C NMR spectra of both samples are almost the same. Thus it has been confirmed that cotton with cellulose I_a and bacterial cellulose with cellulose I_b produce the same crystal form CTA I by the heterogeneous acetylation. Chanzy and Roche[20] studied the change in *Valonia ventricosa* microfibrillar morphology upon the acetylation and saponification by electron microscopy. The structure and orientation for the acetylated and deacetylated microfibrils were identified by selected area diffraction. However, no change could be observed in the fibrillar morphology in both reaction processes. Some significant change in chain conformation and/or packing may occur during solid-state acetylation in the case of bacterial and valonia celluloses, but it is difficult at present to discuss in detail this structural change because the cause of the multiplicities of the resonance lines is unknown and the X-ray diffraction method has not clearly detected such a difference.

In Figure 5, we summarize the transformation process of cellulose I_a and I_b for native cellulose. Cotton and ramie celluloses belong to cellulose I_a, while bacterial and valonia celluloses are assigned to cellulose I_b.[1] The heterogeneous acetylation transforms both groups of native celluloses to the same crystal form CTA I, and these CTA I samples are regenerated to cellulose I_a by heterogeneous saponification. Thus the structural difference in cellulose I_a and I_b disappears during acetylation under the low swelling condition.

Registry No. cellulose, 9004-34-6; cellulose triacetate, 9012-09-3.

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Received November 18, 1986

New Initiator System for the "Living" Anionic Polymerization of *tert*-Alkyl Acrylates

The elegant demonstration[1-3] by a Du Pont Co. research team that the nucleophile-assisted "group-transfer" reaction[4] of silyl ketene silyl acetals could be turned into a "living" polymerization process for alkyl acrylates (and other α,β-unsaturated carbonyl monomers) challenged us to revisit possible pathways toward a "living" anionic polymerization of such monomers. Owing to the general importance of poly(acrylates), it would indeed still be desirable to extend such a "living" control to a higher molecular weight range and especially make it compatible with monomers lacking carbonyl conjugated groups (i.e., styrenes, dienes, heterocyclic monomers, etc.), in order to easily synthesize the corresponding and still unknown block copolymers.

Although many attempts to solve that problem have been reported in the literature,[5-9] none of them has been really successful as yet. In this preliminary communication, we describe a possible answer to that challenge.[10]

The strategy followed here has been to minimize the relative importance of the secondary transfer and termination reactions (usually ascribed to the presence of the

0024-9297/87/2220-1442$01.50/0

Table I
Characteristic Data for the Polymerization of *t*-BA Using the *sec*-BuLi/LiCl System, Initiator Capped with Few Units of α-MeSt

solvent	amt *sec*-BuLi, 10^3 mol mL^{-1}	amt LiCl, 10^3 mol mL^{-1}	[LiCl]/[RLi]	*T*, °C	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$(GPC)/$\bar{M}_n$(calcd)
THF	6.6	0	0	−78	3.61	
THF	6.6	3.90	0.59	−78	1.52	1.50
THF	6.6	6.54	0.99	−78	1.29	1.64
THF	6.6	13.06	1.97	−78	1.30	1.25
THF	6.6	33.46	5.02	−78	1.20	1.30
THF (25)/toluene (75)	3.8	5.0	1.30	−78	1.20	1.38
THF (25)/toluene (75)	3.8	4.66	1.22	−30	1.30	1.40
THF (25)/toluene 75)	3.8	4.66	1.22	0	1.63	1.64

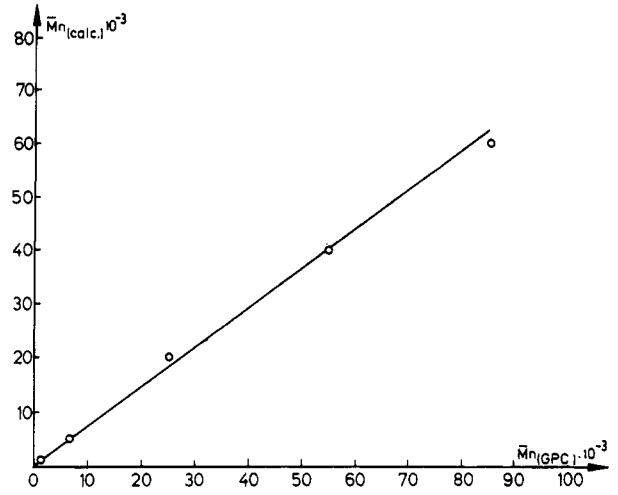

Figure 1. Plot of calculated $\bar{M}_n$ (i.e., grams of reacted *t*-BA per mole of RLi) vs. experimental values obtained from GPC (polystyrene calibration). [LiCl] = 12.66 × 10^{-3} mol L^{-1} and [RLi] = 6.6 × 10^{-3} mol L^{-1} in THF at −78 °C.

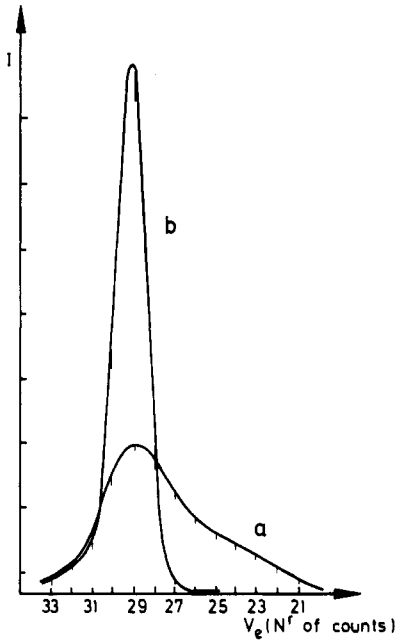

Figure 2. Influence of LiCl on the MW distribution as seen in gel permeation chromatograms: (a) no salt, $\bar{M}_w/\bar{M}_n$ = 3.61; (b) LiCl/RLi = 5.02, $\bar{M}_w/\bar{M}_n$ = 1.20. (Conditions: (a) [RLi] = 6.6 × 10^{-3} mol L^{-1}; (b) [RLi] = 6.6 × 10^{-3} mol L^{-1} and [LiCl] = 33.46 × 10^{-3} mol L^{-1} in THF at −78 °C.)

unhindered carbonyl group and the α-acidic hydrogen), by tailoring the environment of the propagating ion pair. Use of electronically well-balanced ligands is an obvious tactic here, since some decrease in carbanion nucleophilicity might be helpful, whereas it still has to be active enough to accommodate other monomers or reagents afterward. On the other hand, steric hindrance is probably a key tool in reaching that goal, based on the fact that methacrylates behave generally well in anionic "living" processes.[11-14]

Along these lines, we have chosen to coordinate that ion pair with μ-type hindering ligands, e.g., lithium salts with strongly coordinating counteranions, and to test the resulting initiators on bulky esters such as *tert*-butyl acrylate (*t*-BA). The effectiveness of that approach is illustrated by the following typical results, obtained under conventional anionic polymerization conditions (careful purification of reagents, protected reactors, and reagent transfer conditions, although not using a break-seal under vacuum techniques). Polymerization of *t*-BA is performed in THF or in a mixture of THF/toluene (25/75 (v/v)) at −78 °C using an initiator system (RLi) prepared by reacting *sec*-BuLi with a slight molar excess of α-methylstyrene (α-MeSt) at room temperature. *t*-BA is added to the polymerization medium as a dilute solution (10% in THF) rather than as a pure monomer. Polymerizations are extremely fast (ca. 10 min at −78 °C and usually close to quantitative yields, higher than 97%). Figure 1 illustrates the expected linear dependence of $\bar{M}_n$ experimental values vs. the calculated ones, these data being close to 75% of the theoretical values ($\bar{M}_n$(calcd)) expected on the basis of the [M]/[RLi] ratio. The constancy of the $\bar{M}_n$(GPC)/$\bar{M}_n$(calcd) ratio over the whole range of investigated molecular weights might be surprising; nevertheless a similar situation was reported for the living anionic polymerization of methyl methacrylate.[16] Before we conclude a limited efficiency of the catalyst in the present investigation, the molecular weight of the P-*t*-BA samples should be determined by an absolute technique rather than by GPC referenced to standard polystyrene samples.[17] Figure 2 shows the dramatic influence of LiCl on the MW distribution and Table I the influence of the LiCl/anion ratio and of temperature on that same distribution. It is noticeable that brine temperature might be sufficient to maintain an essentially "living" character for the process.

Figure 2 illustrates a piece of information suggesting that the coordintion of the ion pairs to a μ-type hindering ligand (LiCl) is an efficient means of avoiding transfer and termination side reactions. In order to ascertain that opportunity, monomer resumption experiments have been performed in THF at −78 °C; e.g. 0.035 mol of *t*-BA was first polymerized (RLi, 0.88 × 10^3 mol, [LiCl]/[RLi] = 1.70, $\bar{M}_n$ (expt) = 6500, $\bar{M}_w/\bar{M}_n$ = 1.23) and then further added with 0.039 mol of fresh monomer to give a final polymer of $\bar{M}_n$ = 15 400 and $\bar{M}_w/\bar{M}_n$ = 1.24.

Finally, ^{7}Li NMR spectroscopy of "living" PMMA confirms the formation of a complex with LiCl with a seemingly tighter carbanion–lithium pair, judging from the chemical shifts vs. pure LiCl in tetrahydrofuran, i.e., 0.419 ppm for PMMA–Li and 0.147 ppm for the 1:1 PMMA–Li/LiCl complex.

These results illustrate an obviously promising situation that paves the way toward new ω-functional polymers and block copolymers with many different monomers, even in the high MW range.

More important, they allow a rather direct preparation of the corresponding products based on unhindered acrylates. The *tert*-alkyl group used in this study is indeed well-known as a good leaving group in catalyzed hydrolysis and transalcoholysis reactions. Typically, the narrow MW distribution P-*t*-BAs (T_g = 35 °C) so obtained could be converted into the corresponding poly(2-ethylhexyl acrylates) (T_g = −58 °C, 99% conversion from ^{1}H NMR) by heating for a few hours in 2-ethylhexyl alcohol in the presence of a small amount of *p*-toluenesulfonic acid (PTAS) at 150 °C, without chain degradation or broadening of the MW distribution. Still more interestingly, the corresponding poly(acrylic acids) (over 95% conversion from titration, T_g = 140 °C) were similarly obtained upon hydrolysis in the presence of PTAS. If so desired, these transformations can be performed in a one-pot operation immediately following the polymerization.

A more detailed description of these reactions using various initiatiors and conditions, as well as characterization of the different new products accessible through this novel route, will be the subject of forthcoming papers.

Acknowledgment. We are indebted to IRSIA for a fellowship to R. Forte and to Cipari (Luxembourg) and Norsolor (France) for their interest and support. The NMR spectra were obtained at the Creman facility (University of Liège) funded by a grant from the FNRS of Belgium.

Registry No. *t*-BA (homopolymer), 25232-27-3; α-MeSt, 98-83-9; *sec*-BuLi, 598-30-1; LiCl, 7447-41-8.

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Received January 9, 1987