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THE SYNTHESIS OF GRAFT, BLOCK, AND STAR POLYMERS USING ENOLATE-INITIATED ANIONIC POLYMERIZATION

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ABSTRACT

Initiation of the polymerization of methacrylate monomers by enolate ions affords broad opportunities for the design of several types of macromolecules. Alone, or in combination with other techniques, enolate initiation provides routes to the preparation of well-characterized graft copolymers, block copolymers (of both AB and BAB types), star polymers, and H-polymers. The general mechanism of polymerization initiated by lithiated esters and silyl ketene acetals is discussed, and examples are presented of the synthesis of each of the kinds of polymer molecules mentioned above.

INTRODUCTION

In September 1983, the Du Pont Company announced the discovery of a new mechanism for the polymerization of certain monomers, notably methacrylates and closely related compounds, called "group-transfer" polymerization or GTP [1]. Two agents were said to be necessary to cause this type of polymerization to occur; a typical example would use a silyl ketene acetal (SKA) as initiator, the action of which would be stimulated by a catalyst, strongly nucleophilic in solution in tetrahy-

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drofuran (THF), e.g., the bifluoride ion. According to the views expressed then and more recently [2] by the inventors, the trimethylsilyl group of the SKA is said to become transferred to the carbonyl oxygen in the monomer and, by repetition, the trimethylsilyl group remains perpetually attached to the terminal end of the polymer molecule, while the other fragment of the initiator remains at the initiating end. The trimethylsilyl group is, of course, removed during the work-up process to purify the polymer.

The detailed mechanism advanced to account for this type of polymerization has not been universally accepted [3–8], and it seems certain that it cannot be as coordinated a process as originally proposed; it could be that the reaction follows the original scheme in two separate states, as proposed by Müller [4], or it could be essentially an anionic polymerization propagated by an enolate ion [7, 8], in similar fashion to the reactions studied in depth by Lochmann and his colleagues [9–17]. We take the view that the latter is the case, and we refer to the process as enolate-initiated anionic polymerization. From the point of view of exploiting this type of process in order to produce "architect-designed" polymers, the precise nature of the mechanism at the electronic level is not important, provided that the monomer units do indeed become attached to the initiating entity and remain so, and that the chain is "living." Enolate initiation has been developed in our laboratory to furnish methods for the synthesis of graft copolymers, branched homopolymers, and related structures, as described below. The synthesis of block copolymers was reported by the Du Pont group, and we have extended this technique, also.

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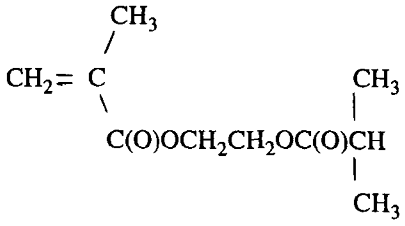
RESULTS AND DISCUSSION

Graft Copolymers

It is easy to see that, if the conditions stated above for enolate initiation are fulfilled, grafts can be developed from a backbone anionically if that backbone contains SKA groups which can be used to initiate the polymerization of an added monomer, such as methyl methacrylate. In principle, it would be possible to arrange for the presence of the SKAs by preparing the backbone by statistical copolymerization [18] of a mixture of monomers, one of which bears SKA groups. However, the SKA moiety is very sensitive to hydrolysis, and it therefore seemed preferable to use a monomer carrying a group which can be a precursor for SKA and to carry out a transformation on the backbone just before attempting grafting.

The classical route to the preparation of an SKA [19] essentially converts an alcohol ROH through the corresponding isobutyryl ester to the SKA, ROC-$(OSiMe_3)C{=}C(Me)_2$. (An alternative procedure is described below.) If the R group contains a vinyl double bond that can be polymerized, it can readily be incorporated in the backbone by (say) radical copolymerization and thus be available for conversion to SKA and subsequent initiation of grafting. This process has been carried out [20] using the monomer 2-isobutyryloxyethyl methacrylate (IBEM) as a component of the backbone and treating the backbone first with lithium diisopropylamide (LDA) and second with chlorotrimethysilane (CTMS) to produce the required SKA groups on the polymer backbone.

[IBEM]



$CH_2{=}C(CH_3)C(O)OCH_2CH_2OC(O)CH(CH_3)_2$

In most of our experiments we employed a backbone comprising approximately 80 mol% styrene and 20 mol% IBEM. The reactivity ratios for the free-radical polymerization of these two monomers were found to be $r_s = 0.71$ and $r_{IBEM} = 0.26$; it was therefore a straightforward matter to prepare statistical radical copolymers containing any desired small proportion of IBEM [20].

The procedure adopted for the preparation of a graft copolymer of styrene and methyl methacrylate was as follows. The necessary statistical copolymer of styrene and IBEM was prepared using free-radical initiation and was carefully dried. A sample (usually about 1 g) was dissolved in THF in a flask closed by a Suba seal, additions of all subsequent reagents being made by syringe. LDA (in THF solution) was then added in a quantity slightly in excess of one equivalent relative to the IBEM residues present. After standing at 0°C for 30 minutes, a solution of CTMS in THF (just over one equivalent relative to the LDA) was added, and the mixture left for 1 hour at room temperature. The polymer was then precipitated, dried, redissolved, and reprecipitated.

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Size-exclusion (gel-permeation) chromatography examination of the product clearly shows that the grafted polymer has a much higher molar mass than does the backbone; moreover, there is no indication whatever of unreacted backbone. Efficient grafting has evidently taken place. This conclusion has amply been confirmed by light scattering, which determines the absolute values of the weight-average molar masses of backbone and grafts.

Branched Homopolymers

Use of the same technique with backbones in which the majority component is methyl methacrylate would be expected to produce branched homopolymers of that monomer, but this has proved to be much more difficult to achieve: following the same procedure as described above led only to gels. Although gel formation could be prevented by carrying out the reactions at much lower temperatures (−75°C), linear homopolymer was formed alongside the desired branched polymer.

Block and Star Polymers

With "living" polymerization systems, the preparation of block copolymers merely requires that monomers be added sequentially. (Of course, it is necessary that the "living" end is actually capable of initiating the polymerization of the new monomer.) This concept has been applied with enolate initiation in order to synthesize the BAB type of copolymer using a difunctional enolate-generating initiator derived from ethylene glycol dimethacrylate by silylation activated by Wilkinson's catalyst [21]. Enolate initiation of the product follows the expected course, giving rise to symmetrical three-block polymers.

If the starting material carry more than two methacrylate functions, a parallel process results in the synthesis of star polymers; these will be homopolymers if only one monomer is employed, but each arm can be a block copolymer if sequential addition of two (or more) monomers is used.

Enolate initiation can be put to good use in the preparation of various types of star polymers; one example follows. Conventional living anionic polystyrene is grown by initiation with butyllithium and terminated by reaction with the dichlorosilane $(Cl)_2Si(Me)R$, where R is a group such as $(CH_3)_2CHC(O)OCH_2CH_2CH_2-$, prepared by reacting the isobutyryl ester of allyl alcohol with dichloromethylsilane. This polymer could be described as polystyrene with an $\rangle$Si(Me)R group at its midpoint. By means of the usual two-stage process, described above, the isobutyryl ester is transformed into SKA, and enolate initiation takes place upon addition of methyl methacrylate and nucleophile, producing a poly(methyl methacrylate) branch attached to the midpoint of the polystyrene chain. This polymer can be regarded as a three-arm star polymer, two arms of which are composed of styrene units and one of methyl methacrylate units [22].

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H-Polymers

McLeish et al. [23–25] made a theoretical examination of the behavior of polymer molecules in the form of the letter H, where both the horizontal bar and the vertical uprights are polymeric in character. It would therefore be of great interest to prepare and study such molecules. The synthesis poses a considerable challenge, but we have sought to solve the problem by harnessing enolate-initiated polymerization, developing the chemistry described above.

Our general strategy was first to prepare the bar by enolate initiate, employing the difunctional initiator described above. The critical step was to terminate the growth of the (horizontal) bar at both ends so as to introduce two sites at each end, all four being equivalent and capable of being transformed into new enolate centers which would initiate the growth of the uprights. This requires the use of an efficient capping reaction, and it was necessary to devote attention to the reactions of model compounds as a basis for the eventual polymer synthesis [26].

CONCLUSIONS

The technique of enolate-initiated anionic polymerization can be applied in versatile fashion to the synthesis of polymer molecules containing desired structural features. Thus, it is possible to prepare block copolymers of both BAB and AB types, star polymers, graft copolymers, and H-polymers by using enolate initiation at a strategic point in the synthesis.

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