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SYNTHESIS AND REACTIONS OF POLYAMINES WITH LIVING CATIONIC END GROUPS

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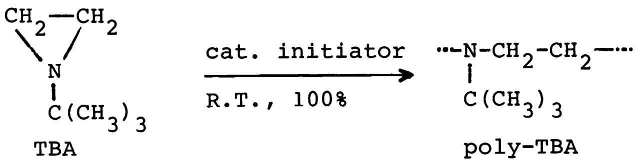
Abstract - The living character (expressed by the ratio k_p/k_t) of the cationic ring-opening polymerization of N-substituted aziridines is strongly influenced by the number and the bulkiness of the substituents on the monomer. Thus, N-tert.butyl aziridine (TBA) has a k_p/k_t value of 10^4 $l.mol^{-1}$ compared with 80 for N-isopropyl aziridine and 4 for N-ethylaziridine. Polymerization of TBA initiated by methyl trifluoromethylsulfonate (methyltriflate) in a mixture of THF and HMPT allows to prepare poly-TBA with well defined molecular weight (up to 100,000) and of low dispersity. The thus obtained polymers give a slow termination reaction which obeys first order kinetics and during which the molecular weight of the polymer remains unchanged. It is therefore assumed to be an intramolecular attack of the growing species by an amino function of its own polymer chain. Because the termination is very slow compared with propagation, it is possible to react the aziridinium ions which are the active chain ends, with a nucleophile before the termination becomes important. This reaction was first checked with a model compound (N-methyl-N-tert.butyl aziridinium triflate) and was then carried out with living poly-TBA. In this way a number of poly-TBA's with different functional end groups were synthesized. They were characterized by 360 MHz ^1H NMR spectroscopy and by GPC. If the nucleophile is part of another polymer chain, block or graft copolymers containing poly-TBA segments are obtained.

Other aziridines showing a high living character are N-substituted propylenimines. Also with these monomers, polymers with predictable molecular weight and well defined end groups can be synthesized. This kind of chemistry allows to form a great variety of block- and graft copolymers containing polyamine segments.

INTRODUCTION

The propagation reaction in the cationic polymerization of N-substituted aziridines is nucleophilic attack of the monomer amino function on the aziridinium ion which is the active species of the polymerization. The resulting polymer, however, also contains amino functions which will compete with the monomer to react with the active species. The result is a non-strained and therefore unreactive ammonium ion. This reaction is an irreversible termination reaction and is the cause of the incomplete conversions that are generally observed in this kind of polymerizations (1-3). If in such a polymerization the initiation is rapid compared to propagation, the maximum conversion of monomer to polymer is determined by the initiator concentration c_o, the initial monomer concentration m_o, and the ratio of the rate constant of propagation to the rate constant of termination k_p/k_t (2). Since transfer to monomer is generally absent, the molecular weights of the polymers are then determined by $\Delta m/c_o$. As reported earlier (3) the values of k_p and k_t are influenced in a different way by the presence of substituents on the monomer. More and bulkier substituents decrease k_t much more than k_p so that the result is a slower polymerization but having a higher living character, thus leading to higher conversions and higher molecular weights. This is illustrated by the observation that the k_p/k_t ratio for N-substituted propylenimines is about two orders of magnitude larger than for the corresponding N-substituted ethylenimines. One of the most striking examples of this phenomenon, however, is shown by N-tert.butyl aziridine (TBA) . This monomer can be polymerized to high molecular weight polymers in quantitative yield (4).



The obtained polymer has some interesting properties: it is a remarkably stable, highly crystalline material with a m.p. of 142°C and it becomes water-soluble when treated with an equimolar amount of acid.

When the ratio k_p/k_t is high (e.g. $>10^3$ $l.mol^{-1}$) and provided a rapid initiation is present the termination only starts when the polymerization is almost quantitative. Consequently, there exists a certain period during which most of the monomer has been polymerized and where the majority of the formed polymer molecules still have an active aziridinium ion as chain-end. This group is a strong electrophile and consequently such polymers are capable to react with nucleophilic compounds leading to polymers with well defined end groups or (if the nucleophile is part of another polymer) to block- or graft copolymers containing polyamine segments.

In the present paper we will first describe the kinetics of the polymerization of TBA in order to confirm that this is a real "living" polymerization, and then report a series of reactions of different nucleophiles with the living poly-TBA.

Kinetics of the polymerization of TBA.

For the kinetic study, triethyloxonium tetrafluoroborate (TEFB) was used as the initiator. The polymerizations were carried out at temperatures between -10 and -40°C in methylene chloride. The concentration of monomer and polymer were followed by ^1H NMR spectroscopy. Figure 1 shows examples of first order plots obtained at different temperatures. The straight lines are in accordance with a fast initiation reaction and absence of termination during the polymerization. In such a system the concentration of growing species remains constant and is equal to the initiator concentration so that the values of k_p can be determined from the slopes according to :

$$\ln m = \ln m_o - k_p c_o t.$$

Values of k_p are listed in Table 1. The activation enthalpy and entropy are shown in Table 2.

TABLE 1. Values of k_p and k_t for the polymerization of TBA in CH_2Cl_2 initiated with TEFB.

Temp. (°C)	c_o ($mol.l^{-1}$)	$k_p \times 10^2$ ($l.mol^{-1}s^{-1}$)	$k_t \times 10^5$ (s^{-1})
-20	0.04	3.5	
	0.03	4.1	
	0.02	4.5	
-30	0.04	1.4	
	0.025	2.2	
-40	0.036	0.60	
	0.018	0.73	
0	0.045	(a) 18.5	1.4
10	0.045	38	3.3
20	0.051	73	5.3
30	0.045	150	13.0

(a) Extrapolated values.

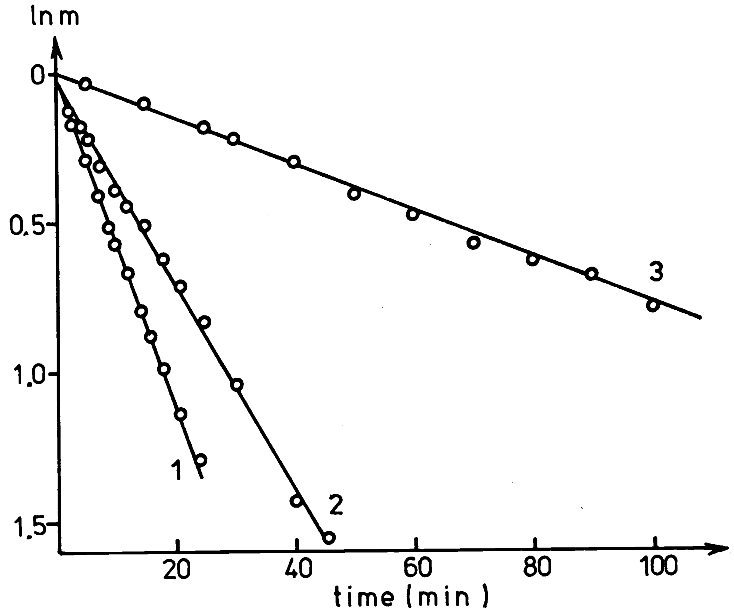


Fig. 1. First order plots for the polymerization of TBA at different temperatures in CH_2Cl_2. [TEFB] = 0.020 mol.l^{-1} ; m_o = 1.0 mol.l^{-1}, temperature -20°C (1); -30°C (2); -40°C (3).

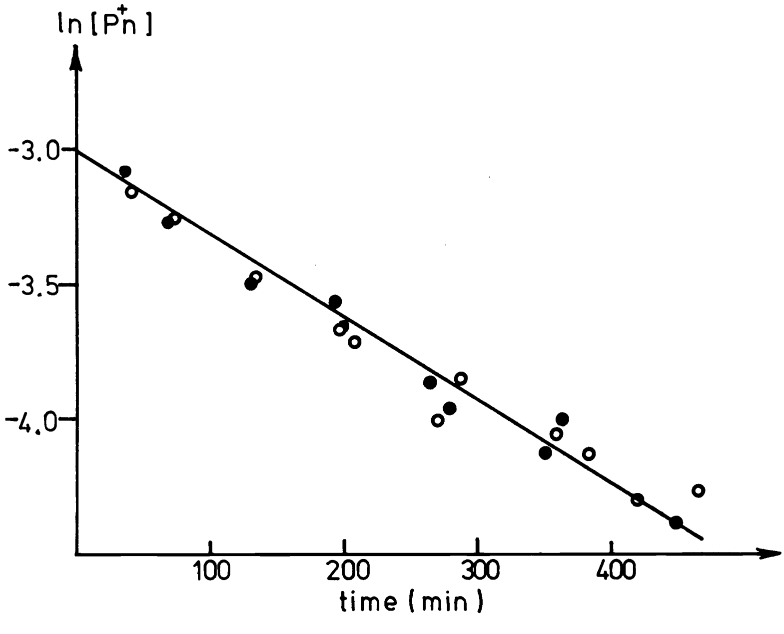


Fig. 2. First order plot for the disappearance of growing species of poly-TBA at 20°C in CH_2Cl_2 [TEFB] = 0.05 mol.l^{-1}, m_o = 0.5 mol.l^{-1} (o) or 1.0 mol.l^{-1} (●).

TABLE 2. Thermodynamic parameters for the polymerization of TBA in CH_2Cl_2 initiated by TEFB.

$\Delta H_p^{\neq}$	46 $kJ.mol^{-1}$
$\Delta S_p^{\neq}$	-88 $J.mol^{-1}K^{-1}$
$\Delta H_t^{\neq}$	46 $kJ.mol^{-1}$
$\Delta S_t^{\neq}$	-168 $J.mol^{-1}K^{-1}$

The kinetics of the termination reaction were also studied by ^1H NMR spectroscopy. The protons of the tert.butyl group of the active species give a singlet at 1.38 ppm. By the use of an internal standard (CH_3CN) the concentration of the active species $[P_n^+]$ could be followed as a function of time. At the low temperatures as used in the experiments of Fig. 1, the concentration did not change noticeably but at 0°C or higher a slow decrease was observed. First order plots give straight lines so that the termination reaction must occur according to first order or pseudo first order kinetics. Intramolecular termination to form a cyclic ammonium salt would lead to first order kinetics according to eqn. (1)(assuming quantitative initiation):

$$\ln[P_n^+] = \ln[P_n^+]_o - k_t\, t = \ln c_o - k_t\, t \qquad (\underline{1})$$

where c_o is the initiator concentration.

An intermolecular termination between the active species and any of the amino-functions of the polymer chains in the solution would lead to pseudo first order kinetics because the amino-functions are present in large excess and their concentration therefore practically remains constant. In this case, however, the rate of termination is given by eqn. (2):

$$\ln[P_n^+] = \ln[P_n^+]_o - k_t[N]t = \ln c_o - k_t\, m_o\, t \qquad (\underline{2})$$

where [N] is the concentration of polymeric amino-functions which is equal to m_o, the initial monomer concentration since the termination becomes important only when the polymerization is virtually quantitative.

In order to distinguish between these two possibilities, the termination kinetics were followed with two different polymer concentrations (starting from different monomer concentrations). The observation that the slope of the plot (Fig. 2) did not change was taken as a proof that the reaction is really of first order and therefore an intramolecular termination is assumed.

Additional evidence for this mechanism is given by the fact that the viscosity of the terminating polymer solution remains constant. Intermolecular termination would lead to branched structures and hence to an increase in viscosity. Also, GPC analysis of the polymer after various degrees of termination, gave the same chromatograms, showing that no branching takes place.

Values of the rate constants of termination at different temperatures are given in Table 1. The activation enthalpy and entropy parameters are shown in Table 2. It is remarkable that the activation enthalpies for propagation and termination are, within the experimental error, equal. The entropy of activation, however, is much more negative for the termination reaction than for the propagation which is in agreement with the assumption that steric hindrance around the polymeric amino-functions, caused by the bulky tert.butyl substituents, is the reason for their low reactivity towards the aziridinium ion.

From these kinetic studies it follows that in this polymerization the k_p/k_t ratio, which is a measure for the living character, is $1.2x10^4$ $l.mol^{-1}$. It may thus be concluded that the polymerization of TBA has a high living character although it is not "immortal". Consequently, reactions at the active species have to be carried out shortly after the polymerization.

Synthesis of living poly-TBA with predictable molecular weight and low polydispersity.

The reaction conditions used for the kinetic study of the polymerization are not suitable for the synthesis of well defined living poly-TBA and subsequent reaction of the active species with nucleophilic reagents. The main reasons are that (1) methylene chloride is not inert towards nucleophiles and (2) when high initiator concentrations are used, with the purpose to obtain low molecular weight polymers, initiation becomes incomplete because the first formed aziridinium salt has a limited solubility in methylene chloride and, as a consequence, the formed polymers do not correspond to the expected ones.

It was found that good results are obtained when the polymerization is carried out in a mixture of tetrahydrofuran (THF) and hexamethyl phosphoric acid triamide (HMPT) with methyl triflate as the initiator (5). Table 3 gives a survey of the results obtained with this system. The obtained molecular weights are close to the calculated values and the polydispersity is low.

TABLE 3. Molecular weights and polydispersity of poly-TBA as a function of m_o/c_o

m_o/c_o	M.W. calculated	M.W. experim.$^{(a)}$	M.W. GPC$^{(b)}$	M_w/M_n
30	2970	3493	3220	1.27
50	4950	5589	5305	1.11
70	6930	7906	7400	1.27
100	9900	10434	10330	1.14
300	29700	34733	35950	1.35

(a) Measured by vapour pressure osmometry in THF at 40°C.

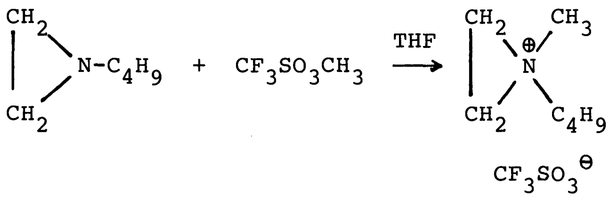
(b) Using calibration curve obtained with polystyrene standards (TSK H_{8000} column, eluent THF).

Also under these new reaction conditions a slow termination reaction (after quantitative polymerization) took place. This was observed by NMR spectroscopy and confirmed by using a solution of "living" polymer to initiate new polymerizations at regular intervals. Analysis of the end products showed that, if new monomer was added after a short time, all initial polymer had reacted to form a polymer with higher molecular weight, as predicted for a real living system. However, as the initiating polymer solution became older, part of the original polymer remained unchanged whereas the newly formed polymer had a molecular weight corresponding to a higher m_o/c_o ratio. Figure 3 shows a number of GPC analysis of polymers obtained by these second monomer addition experiments.

Typically, the polymerizations are carried out at room temperature giving complete conversion within 5 minutes. After addition of the desired nucleophile and another reaction time of 10-15 minutes, the polymer is precipitated in methanol, filtered and dried in vacuo.

Reactions of living poly-TBA with nucleophiles.

The reactions of living poly-TBA were first checked with the model compound N-methyl-N-tert.butyl aziridinium triflate which can be prepared by treating TBA with an equimolar amount of methyl triflate in dry ether at -20°C. Under these conditions, the salt precipitates in crystalline form (m.p. 60°C).



This compound reacts almost instantaneously (at room temperature) with a great variety of nucleophiles such as halide anions, phenolate anion, hydroxide anion etc. with the formation of the corresponding ring-opened products.

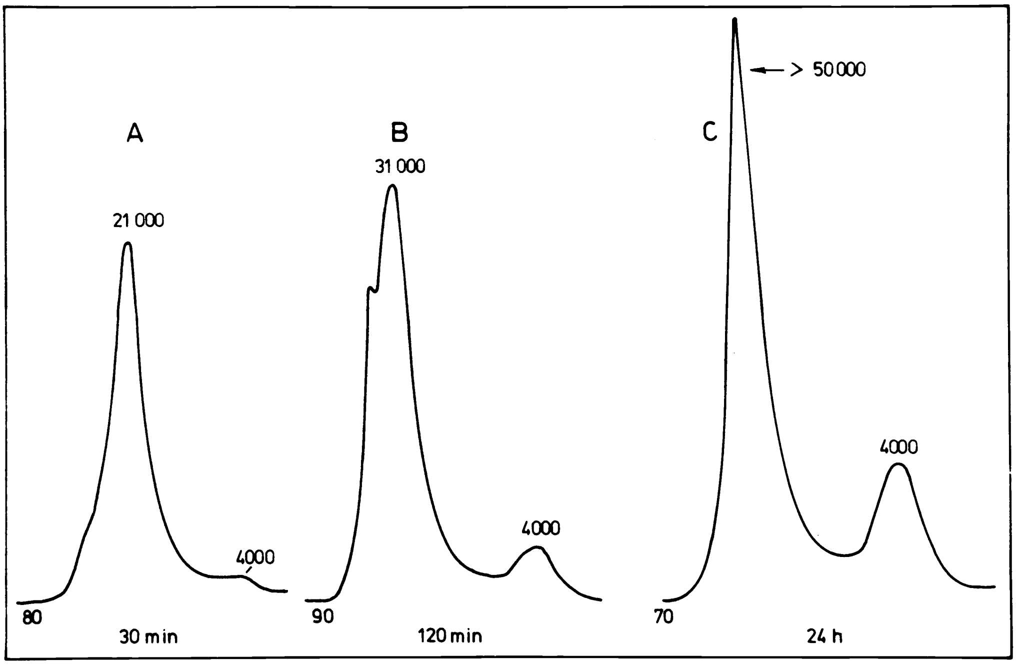


Fig. 3. GPC Analysis of polymers obtained after second monomer additions. New monomer added after A 30 min, B 120 min, C 24 h. m_0 = 0.8 $mol.l^{-1}$, c_0 = 0.020 $mol.l^{-1}$, temperature 20°C, for the new monomer addition: m_0' = 1.0 $mol.l^{-1}$.

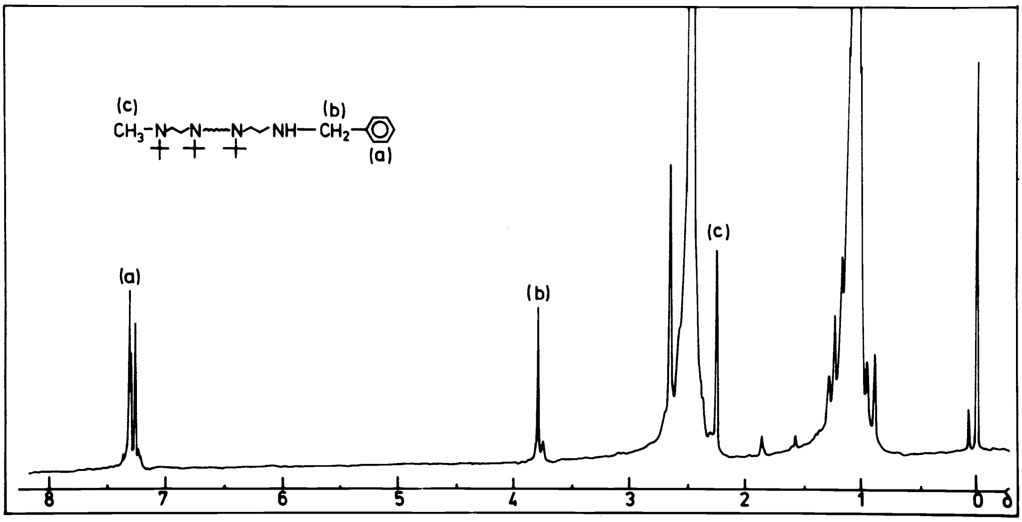
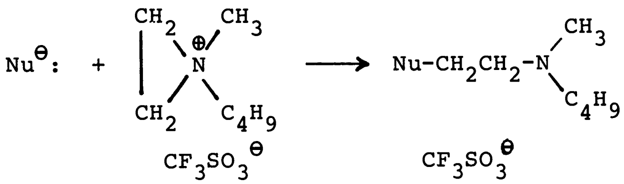
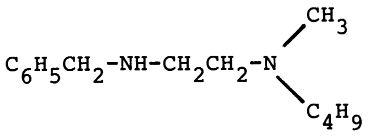
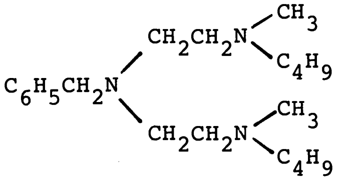


Fig. 4. 360 MHz ^1H NMR spectrum of benzylamine-terminated poly-TBA.



Tertiary amines with little steric hindrance, such as pyridine, lead to a quaternary ammonium salt. With primary amines such as benzylamine, a mixture of mono-adduct and diadduct is obtained:

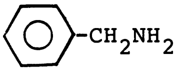
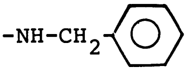
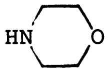
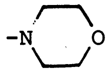
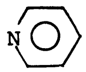
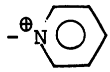
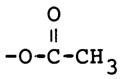
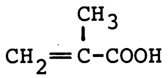
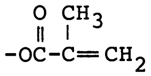




The liberated triflic acid forms an ammonium triflate with one of the amino functions. The reaction with water is very slow but becomes instantaneous on addition of potassium hydroxide. The salt does not react with organic acids but does react with carboxylate anions.

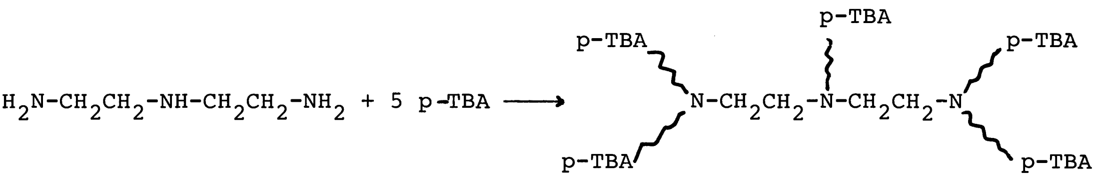
The same behaviour was observed for the living chain ends of poly-TBA and in this way a number of poly-TBA's with different functional end groups were prepared. Table 4 gives a survey of the nucleophiles which have been used and the corresponding end groups which were obtained. The polymers were characterized by ^1H NMR spectroscopy. As an example, Fig. 4 shows the spectrum of the benzyl amine-terminated polymer. Integration of the methyl head group at 2.25 (originating from the initiation reaction) and the benzylic methylene end group at 3.80 ppm, shows that they are present in equimolar amounts which proves that the transformation of the aziridinium group was quantitative.

TABLE 4. Reactions of living poly-TBA with nucleophiles.

Nucleophile	Endgroup
NaOH	-OH
LiBr	-Br
	
	
	
$H_2N-(CH_2)_3-Si(OEt)_3$	$-NH-(CH_2)_3Si(OEt)_3$
CH_3COOH	 $-O-\overset{\overset{O}{\|}}{C}-CH_3$
 $CH_2{=}\overset{\overset{CH_3}{\mid}}{C}-COOH$	 $-O\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{\mid}}{C}{=}CH_2$

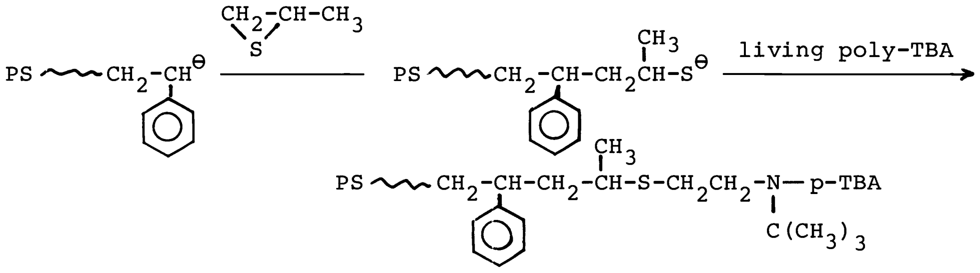
The polymer corresponding to Fig. 4 was obtained by reaction of living poly-TBA with excess of benzyl amine. Reaction with an equimolar amount of benzyl amine gives a mixture of mono-adduct and di-adduct. The presence of the di-adduct was proved by GPC where two peaks are visible: a first one corresponding to the original molecular weight of the living poly-TBA and a second one appearing at an elution volume corresponding to the double molecular weight.

When living poly-TBA is allowed to react with diethylenetriamine, a star-shaped polymer containing up to five poly-TBA molecules is obtained.



Of special interest is the reaction with methacrylic acid. This leads to a poly-TBA carrying a methacrylate end group which is a new type of macromer (macromolecular monomer). Copolymerization of this macromer with other vinyl monomers may lead to polymers with poly-TBA grafts.

Reactions of living poly-TBA with other polymers.
Direct coupling of a living cationic polymer with a living anionic polymer, to produce a block-copolymer, has been described for the case cationic poly-THF - anionic polystyrene (6). Attempts to do an analogous coupling of poly-TBA with polystyrene failed, the end result being a mixture of the two homopolymers. However, when the carbanion of the anionic polystyrene was first converted into a thiolate anion by reaction with propylene sulfide (7), coupling with living poly-TBA was successful giving a block-copolymer polystyrene-poly-TBA.



An A-B-A type of block-copolymer was synthesized by reaction of living poly-TBA with telechelic amino- or carboxy-terminated polymers with poly-butadiene or poly(butadiene-co-acrylonitrile) as the backbone. These commercially available polymers are viscous liquids. The block copolymers are waxy or rubbery substances depending on the ratio of the length of the polymer segments. The formation of block-copolymers was proved by GPC and by NMR analysis.

Living poly-TBA can be used to form well defined graft copolymers by the "grafting onto" method in which the active species of the poly-TBA chains are reacted with polymers containing the appropriate nucleophilic functions. This has been achieved with poly-(2-vinylpyridine) as the "deactivating" polymer. GPC analysis of the reaction mixture showed that poly-TBA is quantitatively bound to the poly-(2-vinylpyridine).

CONCLUSION

Knowing the mechanism of propagation and termination in the cationic ring-opening polymerization of N-substituted aziridines and understanding the factors which influence the rate constants of these elementary reactions, it was possible to choose the right monomer structures to produce polymers with cationic living end groups. This possibility has been investigated in detail for N-tert.butyl aziridine but it is expected that most N-substituted propylene imines, which also show a high living character, will behave in a similar manner. These findings open a wide variety of possibilities to produce block- and graft copolymers, containing polyamine segments.

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