Synthesis and characteristics of polystyryl aluminium derivatives and their reaction with benzoyl peroxide

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Thermal polymerization of styrene in the presence of $AlEt_3$ acting as the chain transfer agent permits the synthesis of polystyryl derivatives of aluminium $(polySt)_nAlEt_{3-n}$(poly St-Al). It is possible to regulate the length of the polymer radical over a wide range ($P_n = 2$–800) by altering the ratio of the monomer to the chain transfer agent. A high degree of substitution of ethyl groups occurs only for styryl derivatives containing relatively low-molecular weight substituents ($P_n = 2$–30). The reaction of polySt-Al with benzoyl peroxide occurs virtually instantaneously even at $0°$ and is accompanied by the formation of free polystyryl radicals. Their continuous formation was regulated by introducing catalytic amounts of pyridine as the electron donor into the reaction mixture. A polySt-Al ($P_n = 30$)–BP–Py system was used as an example of showing that these systems can be very effective initiators of the low-temperature free-radical polymerization of a series of acrylic and methacrylic monomers. The process yields a block copolymer. The data was used for the further development of the synthesis of block copolymers with initiating systems of the poly St-Al-peroxide type under low-temperature free-radical polymerization conditions.

Keywords Organoalumium compounds; benzoyl peroxide; initiation mechanism; electron donors; block copolymers

INTRODUCTION

The processes of homolytic substitution with the participation of a metal atom (in organometallic compounds) by the action of free radicals on a reaction centre at oxygen or nitrogen have recently been investigated[1,2]. This is due to the importance of the practical application of these reactions[3,4]. Organoaluminium compounds are a specific case. The energetic advantage of the interaction with oxygen-containing compounds is so great that the homolytic substitution occurs not only in the reaction with free radicals but also in the ineraction with peroxides over the temperature range which lies below the temperature of their thermal degradation[5-7].

Thus, the combination of organoaluminium compounds with peroxides is very effective in the formation of free alkyl radicals (previously bonded to aluminium) at low temperatures. One of the possibilities of using these initiating systems is the initiation of low temperature free-radical polymerization of vinyl monomers[8-10]. A specific feature of these initiating systems is the fact that the radical activity is displayed by the radical previously bonded to aluminium. This suggests that these systems could be used for the synthesis of block copolymers when one substituent (P) is polymeric. The investigation, the aim of which was the synthesis of block copolymers in a low-temperature free-radical process, consisted of the following stages: (1) the synthesis of organoaluminium compounds with a high molecular weight radical; (2) the study of their reactions with the peroxide and, finally, (3) the elucidation of the conditions permitting the use of these systems for the synthesis of block copolymers[11]. Before discussing

experimental considerations it is advisable to show the reasons for choosing the method of the synthesis of organoaluminium compounds with a substituent of high molecular weight (Al-P). Generally the preparation of Al-P is a difficult task since the usual method for the synthesis of high molecular weight compounds containing an alkali or alkaline earth counterion and therefore an anionic polymerization cannot be used for aluminium alkyls. A particular path for solving this problem is to use the ability of alkyl aluminium compounds $(Alalk_3)$ to participate in homolytic reactions as chain transfer agents[12]. The mechanism of action with $Alalk_3$ consists of the replacement of an alkyl substituent by a free radical. Under conditions of free radical polymerization this process leads to the formation of Al-P. In this work the thermal polymerization of styrene (St) was chosen as a source of high molecular weight radicals. It was carried out in the presence of $AlEt_3$ as the chain transfer agent.

The information available in the literature[12] did not make it possible to select the reaction conditions for the synthesis of polystyryl aluminium derivatives. Firstly, it was necessary to elucidate the extent to which the function of $AlEt_3$ is limited to that of a chain transfer agent even at high conversion, i.e. to establish that the presence of $AlEt_3$ would not prevent a 100% conversion of the monomer.* It was also necessary to determine the relationship between the conditions of the synthesis and the parameters of the polystyryl aluminium being formed, $Al (polySt)_nEt_{3-n}$,**

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* The reaction mixture containing the desired product was used subsequently without additional purification. Hence, the absence of the monomer in the reaction mixture was one of the conditions of the synthesis.

** From now on these compounds are designated as polySt-Al.

Table 1 Isolation of St–MMA block copolymer and its characteristics (10% chloroform solution, 20°C)

| | Polymer mixture 6.8 g | | | | | |
| | Residue | | | Filtrate | | |
Operation	Weight, (g)	Styrene** (%)	$[\eta]$***	Weight, (g)	Styrene** (%)
Reprecipitation into petroleum ether $\dfrac{\text{precipitant}}{\text{solvent}} = 5$	2.3	24.5		3.9	97
Extraction with diethyl ether	1.76	12.5		0.44	75
Fractional precipitation (chloroform-petroleum ether, $\gamma = 0.75$)*	1.6	12.3	0.19		

* γ = precipitant volume/total volume
** Styrene content was calculated by i.r.-spectra from the intensity of characteristic bands at 1603 cm^{-1} (benzene ring vibrations) and 1730 cm^{-1} (vibrations of C=O group in MMA)[14]
*** Chloroform, 25°C

i.e., the number of chains ($\bar{n}$) of polystyryl bonded to aluminium and the degree of polymerization ($\bar{P}_n$) of the polystyryl chain.

In further investigations it was necessary to study the interaction between Al-P and peroxide, i.e., to establish whether a reaction occurs between them at all and whether it is homolytic. The answer to the question of the nature of the radicals formed in this reaction and its temperature range would show whether it is possible to use the initiating systems of the type: organoaluminium compound–peroxide for the synthesis of block copolymers under low-temperature conditions.

This paper deals with the synthesis of styryl aluminium derivatives including those containing high molecular weight substituents and the reaction between these derivatives and benzoyl peroxide (BP).*

EXPERIMENTAL

Solvents were purified in the usual manner and dried over CaH_2. Styrene (St) was washed to remove the stabilizer, dried over $CaCl_2$ and CaH_2, twice distilled under vacuum and pre-polymerized over metal sodium prior to use. Other monomers were purified in the usual manner, distilled under vacuum and pre-polymerized with the $AlBu_3$–BP system. The synthesis of polySt-Al and the subsequent reactions were carried out under conditions excluding air and moisture.

PolySt-Al with $\bar{P}_n = 2$–30 was synthesized in sealed dilatometers under vacuum (120°, 8 days). Preliminary experiments were used to monitor the polymerization kinetics of the reaction mixture at [St]:[Al] = 8–12 and the content of the unreacted styrene. It was established that the conditions used permit quantitative conversion of styrene. Solutions of polySt-Al ($\bar{P}_n = 2$–300) were stored in Schlenk vessels and introduced into the reaction vessel directly from them. PolySt-Al with $\bar{P}_n = 800$ was synthesized in double-chamber dilatometers with a partition and a calibrated neck, which permitted their direct use in further operations. The concentration of 'active' organoaluminium compound was established from the reaction with NEt_3 by evaluating the amount of unreacted amine (by distillation under vacuum and subsequent determination of concentration by titrating

with HCl). The amount of unsubstituted ethyl groups in polySt-Al was established by gas volumetric analysis decomposing the reaction solution with a toluene–butanol mixture and measuring the amount of the gas evolved. *MW* of polySt was determined for decomposed samples of polySt-Al. Analytical characteristics listed in *Table 2* (in Results and Discussion) were obtained in this manner.

After the interaction of polySt-Al with BP the reaction mixture was decomposed with water, the hydroxyaluminium benzoate evolved was filtered off, the precipitate was analysed for the content of benzoate groups and the filtrate was analysed for the content of peroxide and saponified products. The spectra were recorded with an IS-DC-301 spectrometer (in KBr pellets). The polymerization of polar monomers was carried out in single-chamber ampoules with calibrated necks, the catalyst components and the monomer were introduced from Schlenk vessels. The yield was determined from the amount of dry residue (subtracting the amount of polySt taken for the reaction). The isolation procedure and the characteristics of the St–MMA block copolymer are listed in *Table 1*. The presence of homo PMMA in the copolymer and the extent of its separation from homo-polySt were monitored by t.l.c.

RESULTS AND DISCUSSION

Synthesis of polySt-Al

The polymerization of styrene was carried out at 120°C. The concentration of $AlEt_3$ was varied from 7.10^{-3} to 7.10^{-1} mol l^{-1} at constant initial monomer concentration (6 mol l^{-1}), with toluene as solvent. In all cases the reaction proceeds until the monomer is completely consumed (*ca.* 8 days). This was established from dilatometric measurements for oligomer samples with $\bar{P}_n = 2$–4 exhibiting relatively low viscosity and the determination of polymer yield according to the amount of dry residue. During the reaction $AlEt_3$ is completely transformed into compounds containing polystyryl groups at the aluminium atom. This conclusion was based on the maintenance of the amount of active Al–C bonds with a simultaneous decrease in the content of ethyl

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* Some results of this investigation were reported in ref 13.

Table 2 Synthesis of polystyryl aluminium derivatives[a]. [St] ~ 6 mol l⁻¹, 120°C, 8 days, toluene was used as solvent

N	Conditions of synthesis				Characteristics of polySt–Al							
	AlEt₃ concentration mol l⁻¹	$\frac{[St]}{[Al]}$	Concentration (mol l⁻¹)[b]	% of remaining Et groups from theory	MW of polystyrene Found[c]	$\bar{M}_\eta \cdot 10^{-3}$	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w \cdot 10^{-3}$	Calculated[d]	$\bar{M}_w/\bar{M}_n$	$\bar{P}_n$	Number of polystyrene groups[e] $\bar{n}$
1	0.75	8	0.71	13	233	25	18	26	300	—	2	2.6 ($\bar{n}'$)
2	0.50	12	0.48	27	355	78	52	109	540	—	4	2.2
3	0.11	55	0.10	40	3000	210	161	316	2500	—	30	1.8
4	0.015	400	0.014	—						1.5	300	1.5 ($\bar{n}'$) / 2.2 ($\bar{n}''$)
5	0.007	850	—	—						2.0	800	1.0 / 1.6
6	without Al	without Al								2.0	2000	

[a] Experiments were repeated many times
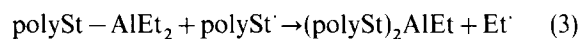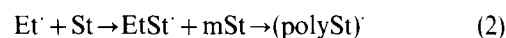[b] Method of determination see Experimental section
[c] The *MW* for samples 1 and 2 was found cryoscopically and by g.p.c., *MW* of sample 3 was found by t.l.c. with reference samples and that of samples 4–6 was found by g.p.c.
[d] From equation (4)
[e] The $\bar{n}$ value in experiments 1–3 was obtained by analysing the reaction product by a gas volumetric method and $\bar{n}'$ and $\bar{n}''$ in experiments 4 and 5 were calculated according to equation (4) by using the values of $\bar{M}_\eta$ and $\bar{M}_n$, respectively

groups in the final product as compared with AlEt₃* (see *Table 2*). The low molecular weight samples 1 and 2 (*Table 2*) taken as examples show that two of their ethyl groups are completely substituted and the third group is partially substituted.

According to our experimental data and the information in the literature[12] the course of the process can be expressed by the equations

$$(polySt)' + AlEt_3 \rightarrow polySt - AlEt_2 + Et' \qquad (1)$$

$$Et' + St \rightarrow EtSt' + mSt \rightarrow (polySt)' \qquad (2)$$

$$polySt - AlEt_2 + polySt' \rightarrow (polySt)_2AlEt + Et' \qquad (3)$$

The study of the *MWD* of low molecular weight samples 1–3 (*Table 2*) by t.l.c. with reference samples and by gel permeation chromatography (g.p.c.) showed the absence of the fraction corresponding to high molecular weight polySt that could be formed during thermal polymerization without the participation of AlEt₃. The molecular weight of the main fraction of oligomers corresponds to the values obtained cryoscopically.

Hence, all these facts show that during polymerization virtually all the styrene is transformed into polySt-Al and the *MW* of the polymer chain is determined by the reaction of chain transfer to AlEt₃ (at 100°C K_{tr} to AlEt₃ is 17[12]). The results obtained for aluminium oligo-derivatives show that all the ethyl groups in AlEt₃ exhibit approximately equal reactivities.

The determination of a relationship between the concentration conditions of the process and the values of $\bar{P}_n$ and $\bar{n}$ gave the following equation confirmed by the data given in *Table 2* (samples 1–3)

$$\bar{P}_n = \frac{[St]}{[Al]\bar{n}} \qquad (4)$$

It can be seen that the experimental values of *MW* and those calculated by using equation (4) are in fairly good agreement.

The determination of the degree of substitution of ethyl groups (i.e. the $\bar{n}$ value) for high molecular weight products (samples 4 and 5) cannot be carried out experimentally. A tentative characterization of these compounds, according to their $\bar{n}$ value, can also be obtained from equation (4). In the cases investigated the limiting value of $\bar{n}$ is unity. The decrease in the reactivity of ethyl groups in polySt-Al with the degree of substitution is probably due to the shielding effect of the long polymer chain. Its length, in turn, is determined by the competition of reactions occurring with and without the participation of AlEt₃, i.e., is directly related to the concentration of the transfer agent. Hence, it should be concluded that it is impossible to obtain polySt-Al containing long chains and at the same time exhibiting a high degree of substitution of ethyl groups.**

These relationships permit the choice of concentration conditions for the synthesis of polystyryl derivatives of alumininium. Thus, the low limit of the AlEt₃

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* The method for the determination of the concentration of polySt-Al and the content of ethyl groups in it is described in Experimental section.
** It will be shown that the use of incompletely substituted derivatives ensures the synthesis of block copolymers.

concentration corresponds to the characteristics of the product approaching the limiting characteristics; these are the length of the polymer chain and, correspondingly, the value of $\bar{n}$ close to unity. Suitable conditions are partly determined in further work with the polySt-Al solutions, dependent on the concentration of the Al–C bond and on solution viscosity. On the whole the results of this investigation indicate that the synthesis of polystyryl aluminium derivatives by a homolytic process is possible. Presumably, the driving force for this reaction is the strength of the Al–St bond which is greater than that of the Al–Et bond in AlEt$_3$ owing to the withdrawal of electrons from the phenyl nucleus[3].

Investigation of the reaction of polySt-Al with benzoyl peroxide

Even relatively low molecular weight polySt-Al ($\bar{P}_n = 2$–30) is a weaker Lewis acid than aluminium alkyls (even with $R = C_{14-16}$). It is impossible to establish visually the decrease in the Lewis acidity because distinct colour transitions with methyl violet as an indicator are absent. This rules out the possibility of detecting active organoaluminium compound by the 'indicator' method. Strong Lewis bases, in particular amines of the fatty acid series, form donor–acceptor complexes and this fact was used to determine quantitatively the content of active Al–C bond. In a similar way to aluminium alkyls, polySt-Al ($\bar{P}_n = 2$–30) reacts irreversibly with BP. The reaction is virtually instantaneous even at $0°$–$20°C$† and corresponds to the stoichiometry of Al:BP = 1:0.75 (0.8), i.e., approximately 4:3. In contrast to aluminium alkyls, for

polySt-Al the reaction proceeds to completion only when a large excess of the peroxide is present. In this case complexation between the final products and the initial organoaluminium compound probably prevents further interaction with the peroxide due to the small amount present or conditions of precise stoichiometry (*Table 3*).

The interaction of polySt-Al with BP proceeds preferentially at the Al–St bond and passes through the stage of formation of free polystyryl radicals. *Figure 1* shows the densitograms of a polySt sample ($\bar{P}_n = 30$). Comparison of curves 1 and 2 representing the *MWD* of the sample before and after the reaction with BP, respectively, shows the shift of the *MW* maximum towards larger values. This effect can take place only when polystyryl radicals are present and subsequently recombine. The Al–Et bond participates in the reaction only to a slight extent (3–5% of the initial amount).

Free benzoate radicals are not formed in the reaction, as is shown by the absence of CO_2 and the virtually complete balance for benzoate groups (*Table 4*).

In accordance with the established stoichiometry (Al:BP = 4:3) and the isolated products it could be

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† Investigations at lower temperatures were not carried out owing to high viscosity of the experimental solution.

Table 3 Stoichiometry of the reaction of polystyrylaluminium with benzoyl peroxide (15 min, 0°C, toluene was used as solvent)*

Degree of poly-merization, $\bar{P}_n$	Al : Bp molar ratio	Amount of peroxide found, % of the initial amount
	1 : 1	26
2	1 : 1	25**
	1 : 2	125
	1 : 0.75	8
4	1 : 1	20
	1 : 1.5	74
	1 : 0.8	5
30	1 : 1	16
	1 : 2	117

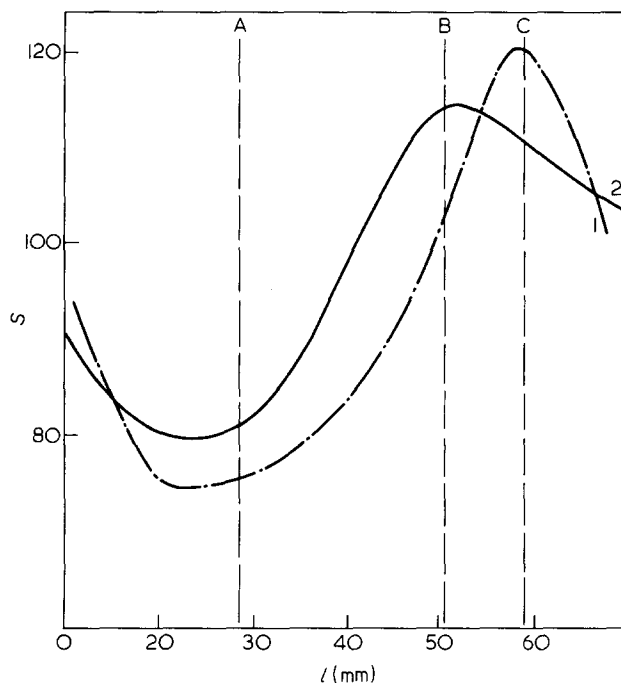* Average values for several experiments
** After 18 h

Figure 1 Densitogram of a polySt sample 1 — initial polySt, 2 — after reaction with BP: positions of reference samples ('waters'-narrow fractions) of polySt and their *MW* (A) 1.10^4, (B) 5.10^3, (C) 2.10^3; S — degree of absorption, l — plate length

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Table 4 Products of the interaction of polystyrylaluminium and benzoyl peroxide* ([BP] = 0.18 mol l^{-1}, 0°C)

$\bar{P}_n$	PolySt–Al concentration mol l^{-1}	Al : BP molar ratio	Amount of benzoate groups found in reaction products, % from theoretical value			Balance for benzoate groups, % from theoretical value
			Aluminium benzoate	Saponified product	Unreacted BP***	
4	0.5	1 : 0.75	80	8	8	96
30	0.05**	1 : 0.80	82	9	5	96

* Average values for several experiments
** Viscosity of the reaction medium markedly affects the quantitative composition of reaction products. Hence, when the interaction of polySt–Al ($\bar{P}_n = 30$) with BP was investigated, more dilute solutions of the organoaluminium compound were used than for polySt–Al ($\bar{P}_n = 4$)
*** At the Al : BP ratio of 4 : 3 the reaction does not proceed to completion (*Table 3*)
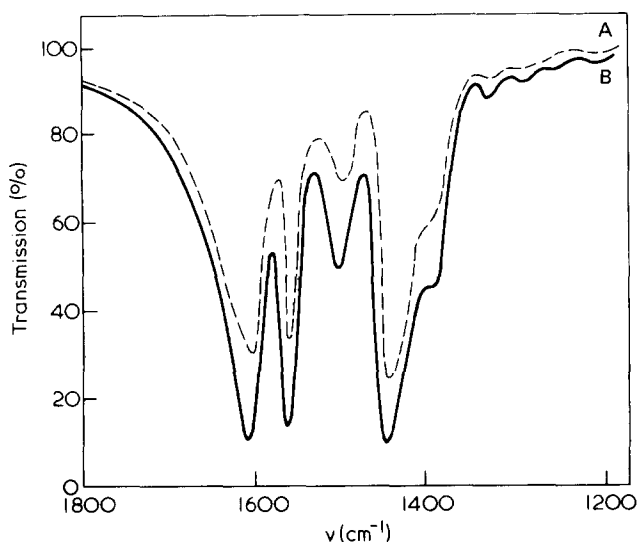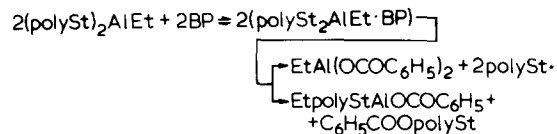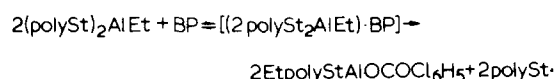
Figure 2 I.r. spectra of products of the reaction of BP with (A) AlEt$_3$ and (B) polySt—Al

Table 5 Reaction of polySt—Al ($\bar{P}_n$ = 30) with benzoyl peroxide in the presence of an electron donor [ED] : [Al] = 50; [BP] : [Al] = 2; 15 min, 0°C, toluene was used as solvent*

ED	Residual peroxide, %	Remarks
MMA	2.7	Excess of peroxide used in the reaction at the Al : BP ratio >4 : 3 is not included in the column 'residual peroxide'
EA	9.0	
Py	95.0	
MMA	63.0	AlEt$_3$—BP; [BP] : [Al] = 0.5; [ED] : [Al] = 50; 0°C
EA**	92.0	ditto, [ED] : [Al] = 25; 25°C

* Order of reagent introduction was always the same: AlR$_3$ + ED + BP

** Taken from references 8 and 9

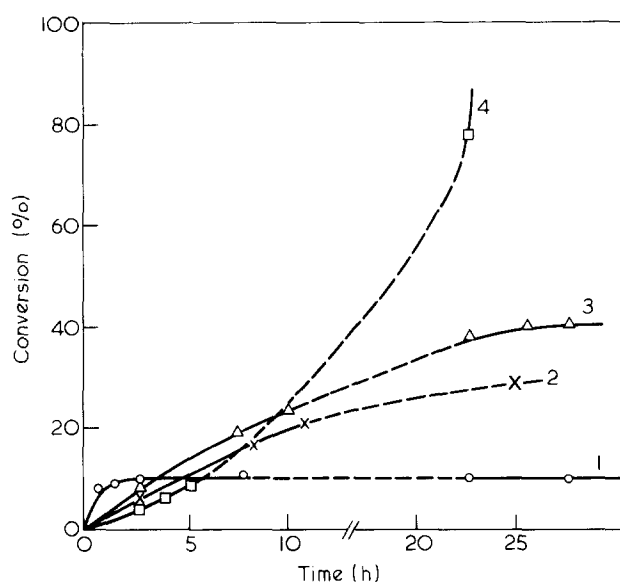expected that both aluminium mono- and di-benzoates will be formed. The i.r. spectra of dihydroxyaluminium benzoate obtained in the reaction of AlEt$_3$ with BP and subsequent decomposition of the reaction mixture with water (*Figure 2*, spectrum A) and hydroxyaluminium benzoate obtained in the reaction of polySt-Al with BP after an appropriate treatment of the reaction mixture (*Figure 2*, spectrum B) show that the intensity of the characteristic absorption bands of COO$^-$ groups (at 1560 and 1440 cm^{-1}) is much greater for spectrum B. This confirms the above suggestion (in both cases identical weight portions of aluminium benzoate were used).

These results suggest the following general scheme for the process

2(polySt)$_2$AlEt + BP $\rightleftharpoons$ [(2 polySt$_2$AlEt)·BP]$\rightarrow$

2EtpolyStAlOCOCl$_6$H$_5$+ 2polySt·

2(polySt)$_2$AlEt + 2BP $\rightleftharpoons$ 2(polySt$_2$AlEt·BP)$\rightharpoondown$

$\rightarrow$EtAl(OCOC$_6$H$_5$)$_2$ + 2polySt·

$\rightarrow$EtpolyStAlOCOC$_6$H$_5$+

+C$_6$H$_5$COOpolySt

This investigation showed the possibility of using a combination of polySt-Al with BP as the initiator of low temperature free-radical polymerization of monomers of the acrylic and methacrylic series. It was also established that when a two-component system is used, polymerization stops long before the monomer is consumed as a result of the fast consumption of the components of the initiating system. It was found that the interaction rate of the components, i.e., the rate of the formation of free radicals, could be monitored by introducing catalytic amounts of the electron donor (ED) into the reaction mixture. Much lower Lewis acidity for polystyryl derivatives than that of aluminium alkyls is indicated by the fact that the introduction of a relatively weak ED, in particular, ethyl acetate (EA) or methylmethacrylate (MMA) does not affect the rate of

Figure 3 Polymerization by the polySt—Al ($\bar{P}_n$ = 30)—BP system with toluene as solvent, 0°C, [Al] = 2.10^{-2} mol l^{-1}; [BP] = 3.10^{-2} mol l^{-1}. 1 — [MMA] = 6.6 mol l^{-1}, without ED; 2 — [MMA] = 3.0 mol l^{-1}, [Al] : [Py] = 1 : 1; 3 — [2-ethylhexyl-methacrylate] = 3.0 mol l^{-1}, [Al] : [Py] = 1 : 1; 4 — [methylacrylate] = 6.0 mol l^{-1}, [Al] : [Py] = 1 : 2

reaction with BP and indeed is extremely fast in this case‡. Only the presence of a very strong electron donor, pyridine (Py), slows down this interaction.

These data are shown in *Table 5* and the results for the AlEt$_3$–BP system are shown for comparison.

In accordance with model experiments, effective initiating systems were obtained by using three-component systems: PolySt-Al–BP–Py. The data in *Figure 3* show the initiating ability of this system for a number of monomers taking as an example polySt-Al ($\bar{P}_n$ = 30). The analysis of the product formed in the polymerization of MMA showed that it is a block copolymer. These data were used for the development of the synthesis of block copolymers in a low-temperature free-radical process occurring under the influence of systems of the type Al-P–peroxide.

‡ The complexing ability of ED and polar monomers with respect to aluminium alkyls has been described elsewhere[8,9].

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