Synthesis of block copolymers by a low-temperature free-radical mechanism using systems of the polystyrylaluminium–peroxide type

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Block copolymers of styrene and a polar monomer (acrylates, methacrylates and acrylonitrile) can be synthesized at low temperatures (20° to minus 20°C) by a free-radical mechanism using initiating systems of the type: polystyrylaluminium (poly St-Al)–peroxide. The degree of polymerization ($\bar{P}_n$) of the styryl substituent in the polySt-Al component had values 30, 300, 450 and 800. Benzoyl peroxide and dicyclohexylperoxydicarbonate were used as peroxide components. The effect of the concentration and nature of the components of the initiating system, catalytic amounts of the additional electron donor component, pyridine, and temperature on the kinetics of the process were investigated. The kinetic dependence makes it possible to consider the formation of free radicals in terms of the donor–acceptor reactions in which all the components of the system including the monomer take part. Synthesis of a block copolymer with MMA was taken as an example to show the relationships between the conditions of the process and the characteristics of the product. The data on molecular weight distribution (*MWD*) and the compositional distribution according to *MW* (pyrolysis and gel permeation chromatography) show that the main product is the ABA block copolymer where A is the styrene block and B is the MMA block. This structure is formed owing to the conditions of the process: initiation by polystyryl radical and recombination as the dominant chain termination mechanism. This structure cannot be formed under the conditions of anionic or radical (polyperoxide) initiation.

Keywords Organoaluminium compounds; benzoyl peroxide; polymerization mechanism; block copolymers; electron donors

INTRODUCTION

In recent years great attention has been focussed on the problems of the preparation of new polymer compositions, in particular, compositions based on block copolymers. Methods for their preparation are being widely developed and in some processes the polymerization of various types is carried out consecutively: anionic–cationic polymerization[1], anionic-free-radical polymerization[2] etc.

One of the new methods suggested for the synthesis of block copolymers is their preparation under low-temperature conditions by free-radical polymerization with systems comprising an organoaluminium compound with a high molecular radical and a peroxide[3,4].

It is possible to use these systems for the initiation of polymerization because the interaction between their components is accompanied by the formation of high-molecular-weight free radicals. When the reaction is carried out in the medium containing a monomer of the acrylic or methacrylic series it also polymerizes and a block copolymer is formed[5].

This paper presents the results of the investigation into the formation of block copolymers with systems based on polystyryl aluminium derivatives (polySt-Al) with the degree of polymerization ($\bar{P}_n$) of the polymer substituent ranging from 30 to 800, and a peroxide. The kinetic relationships of the polymerization in conjunction with the results of the model experiments permitted the formation of some concepts concerning the significance of the donor–acceptor reactions in these systems and thus provided the basis for selecting the conditions for the synthesis of the block copolymers.

EXPERIMENTAL

The preparation of solvents, monomers, Py and BP and the synthesis and analysis of polySt-Al have been described in detail previously[5]. In all experiments polymerization was carried out in the absence of air and moisture. Solutions of polySt-Al ($\bar{P}_n = 30, 300$) in toluene were introduced from Schlenk vessels. Polymerization was carried out in a single-chamber 50 ml dilatometer with a calibrated capillary. PolySt-Al with $\bar{P}_n = 450$ and 800 was synthesized in two-chamber dilatometers with a partition and a calibrated capillary. This permitted their direct use in the synthesis of block copolymers. The introduction of components was similar in all the experiments. A calculated amount of pyridine solution in toluene was added to polySt-Al in the dilatometer. The contents of the dilatometer were maintained at room temperature for 30 min, thermostatically controlled at experimental temperature and the peroxide–monomer

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solution was introduced at the same temperature. The polymerization was halted by precipitating the polymer into petroleum ether acidified with HCl. In the kinetic experiments the process was carried out to 20–25% conversion. The yield was calculated from the dry residue taking into account the amount of polySt (from polySt-Al) taken for the reaction. The removal of the homopolymer from the St–MMA block copolymer was carried out by selective extraction. Homo-polySt was removed by successive treatments of the polymer mixture with diethyl ether and cyclohexane. Homo-PMMA and the block copolymer with low styrene content were removed by extraction with acetonitrile[6]. The styrene–butylacrylate block copolymer was freed of homopolymers and isolated by fractional precipitation in a toluene–ethanol system. *Table 2* (in Results and Discussion section) lists the characteristics of the fraction; $\gamma = 0.75–0.77$* of its yield is about 70% of the weight of the block copolymer. The purity of the isolated block copolymers was checked by t.l.c.[7]. The total styrene content in the block copolymer was established by i.r. spectroscopy (UR-20)[8] and by pyrolysis chromatography. The *MWD*'s of the block copolymers were obtained by gel permeation chromatography (g.p.c.) with a model KhZh-1302 chromatograph by a method used for block copolymers[9].

The complexation constant K_{equil} for the reaction of polySt-Al ($\bar{P}_n = 4$) with THF was determined by i.r.-spectroscopy (UR-20) with all-sealed NaCl cells, $d = 0.0276$ and 0.0100 cm). The reaction:

$$\text{polySt-Al} + \text{THF} \overset{K_{\text{equil}}}{\rightleftarrows} (\text{polySt-Al}\cdot\text{THF})$$

was used to calculate

$$K_{\text{equil}} = \frac{[\text{polySt-Al}\cdot\text{THF}]}{[\text{polySt-Al}]\cdot[\text{THF}]}$$

by using the established equilibrium concentrations of THF bonded in the complex and free of the complex. The latter concentrations were determined from experimentally found extinction coefficients (E_0).

The E_0 values for symmetrical and asymmetrical vibrations of the C–O group of free and bonded THF are shown below in *Table 1a* (benzene, 25°C).

Table 1a E_0 values for symmetrical and asymmetrical vibrations of C–O group of free and bonded THF

C–O	ν cm^{-1}	E_0 l/mol. cm
Free	*a* 1075	170
	s 912	44
Bonded	*a* 1008	143
	s 858	189

To determine the E_0 bond coefficients the solutions of $2 < [\text{polySt–Al}]_0/[\text{THF}]_0 < 3$ and $[\text{THF}]_0 = 0.06–0.17$ mol l^{-1} were used
The value of K_{equil} was calculated for solutions $1 < [\text{polySt–Al}]_0/[\text{THF}]_0 < 1.3$ at the same $[\text{THF}]_0$ concentration

RESULTS AND DISCUSSION

The method for the preparation of polySt-Al has been described previously[5]. *Table 1b* gives the data characterizing the polySt-Al compounds used in this work: the number of polystyrene chains bonded to aluminium ($\bar{n}$) and their $\bar{P}_n$**. Samples 1–4 in *Table 1b* are designated as polySt-Al ($\bar{P}_n = 30$, 300, 450 and 800, respectively).

Table 2 contains information on the polymerization of methylmethacrylate (MMA), ethylhexylmethacrylate (EHMA), methylacrylate (MA), butyl acrylate (BA) and acrylonitrile (AN) with polySt-Al–peroxide systems in the presence of pyridine (Py) as the electron donor (ED). The part played by Py in initiation will be considered in detail below and it should be noted that the use of two-component systems is ineffective and polymerization stops relatively rapidly†. Benzoyl peroxide (BP) and dicyclohexylperoxydicarbonate (PC) were used as peroxides.

The results show that polymerization can occur up to quantitative monomer conversion in the temperature range +20°C to −20°C. The process is accompanied by the formation of a high molecular weight block copolymer. For AN the reaction can also proceed in the absence of Py. A possible reason for the difference in the behaviour of MMA and AN will be considered below. For systems with polySt-Al ($\bar{P}_n = 30$ and 300) virtually all the monomer polymerized forms a block copolymer. For systems with $\bar{P}_n = 450$ and 800 the content of the homopolymer of the polar monomer is somewhat higher and for $\bar{P}_n = 800$ (experiment 12 in *Table 2*) it amounts to about 25% of the total amount of polymerized MMA. The formation of a homopolymer can be related to the

Table 1b Characteristics of the poly St–Al component of the initiating system

		Polystyrene						
					$M_w{}^b \cdot 10^{-3}$			
N	$\bar{P}_n$ Poly St–Al	$\bar{n}$ Amount of polySt groups in poly St–Al	$[\eta]$	$\bar{M}_\eta \cdot 10^{3a}$	$\bar{M}_\eta$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	30	1.8	–	–	–	3^c	–	
2	300	1.5	0.20	29	25	18	26	1.45
3	450	1.4	0.27	43	–	–	–	–
4	800	1.0	0.41	78	99	52	109	2.0

[a] Calculated from the equation $[\eta] = 1.12\cdot10^{-4}\,M^{0.73}$ [10]
[b] Determined by g.p.c.
[c] Determined by thin-layer chromatography (t.l.c.) with reference samples (PolySt from decomposed samples of PolySt–Al)

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* γ is the ratio of the precipitant volume to the total volume

** The general formula of polystyryl derivatives Al is $(\text{polySt})_n$ Al Et_{3-n}

† This is particularly pronounced for systems with $\bar{P}_n = 30$

Table 2 Polymerization of acrylates and methacrylates with the poly St–Al–peroxide–pyridine system. Toluene is used as solvent

		Monomer	Poly St–Al		Peroxide						Characteristics of the block copolymer	
N	Monomer	conc., mol. l−1	$\bar{P}_n$	Conc. x 10^2 mol. l−1	Type	Conc. x 10^2 mol. l−1	$\frac{[Py]}{[Al]}$	*T* (°C)	Time (days)	Conversion, (%)	[η] ***	% of polar monomer****
1	MMA	3	30	5	BP	5	1	0	4	46	0.19	87.7
2	EHMA	3	30	2	BP	3	1	0	1	38	–	–
3	MA	6	30	2	BP	3	1	0	1	76	–	–
4	MMA	6	300	0.5	BP	4	1	0	4	27	1.34	74.5
5	"	6	300	0.5	PC	4	1	0	4	20	–	–
6	"	6	300	0.5	PC	4	20	−20*	4	10	–	–
7	"	6	300	0.5	BP	2	1	20	4	100	–	–
8	BA	3.5	300	0.5	BP	4	1	0	19	58	1.60	78.2
9	AN	6	300	0.5	BP	4	without Py	0	0.5	11	–	–
10	MMA	4	450	0.3	BP	4	1	0	3	12	–	–
11	"	4	450	0.3	PC	4	20	0	3	26	–	–
12	"	4	800	0.24	BP	5	50	0	7	17**	1.80	72.0
13	BA	3.5	800	0.24	BP	4	30	0	25	46	2.64	77.3

* Under these conditions polymerization by a system with BP does not proceed

** Homo-PMMA constitutes 25% of the polymerized monomer

*** Measured in chloroform at 25°C after the removal of homopolymers (monitored by t.l.c.)

**** According to i.r. spectra[8]

increase in the number of residual Et-groups with the propagation of the polystyrene chain of the aluminium component. However, the amount of the homopolymer is much lower than could be expected from the amount of the residual Et groups assuming equal probabilities of breaking of the Al–Et and Al–St bonds in the reaction with BP. The data (yield of the block copolymer is much higher than that of the homopolymer) distinctly show that the formation of polystyryl radicals is preferable to that of ethyl radicals. This may be due first of all to the lower strength of the Al–St bond. However, this concept is at variance with the previous assumption that the Al–St bond is more stable than the Al–Et bond, which ensures the occurrence of a relatively unusual radical reaction consisting of replacement of a less active radical with a more active radical[5]. It seems appropriate not only to report the exact experimental results but also to attempt to account for these discrepancies.

It is well known that for organoelementary compounds with aromatic substituents an additional bond may be formed between the central atom and the ligands owing to the electron donation from the ligands[11–13]. The introduction of an additional electron donor (ED) leads to the cessation of this 'internal' complexation as has been shown, in particular, for organoboron compounds (u.v. spectroscopy)[11]. It is conceivable that this, in turn, leads to the decreasing strength of the aromatic compound–metal bond.

Similar relationships can also exist for organoaluminium compounds. Thus, the formation of polystyryl derivatives during the synthesis reflects the increasing strength of the Al–St bond as compared with the Al–Et bond. The interaction with the peroxide, which is a donor–acceptor reaction, is accompanied by a change in the bond strength of the organoaluminium compound. As a result, the breaking of the Al–St bond becomes energetically more favourable than that of the Al–Et bond.

All these facts and concepts suggest that incompletely

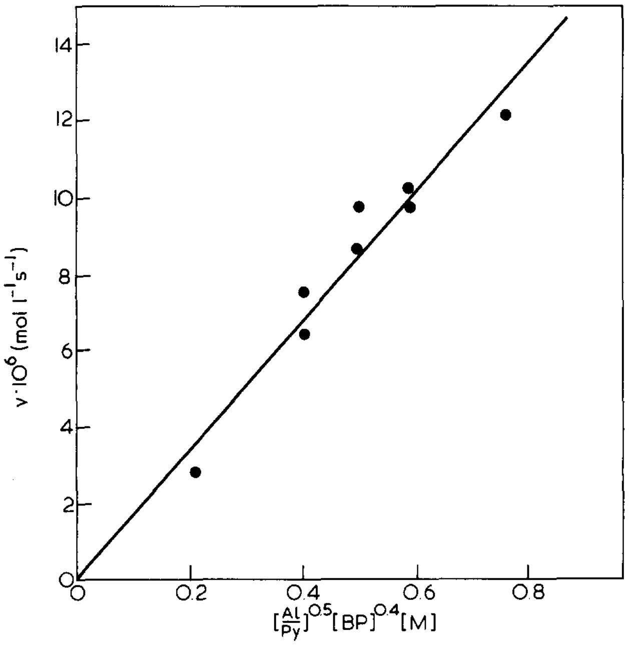


Figure 1 Polymerization rate of MMA vs. concentration of components of the initiating system polySt–Al ($\bar{P}_n$ = 30)–BP–Py; toluene was used as the solvent, 0°C

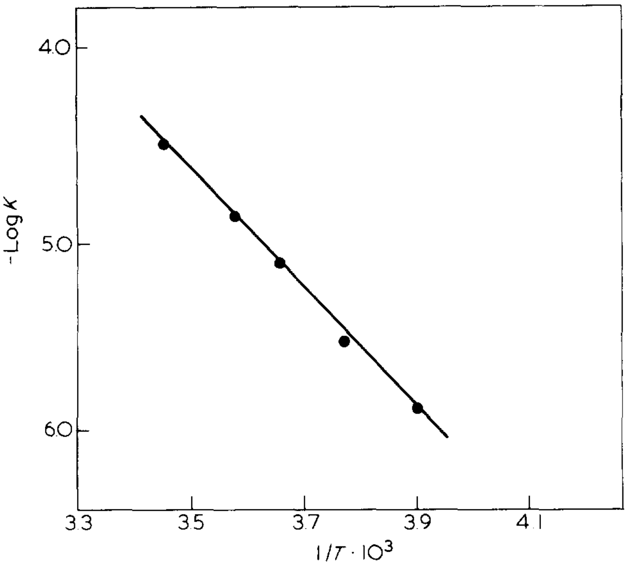


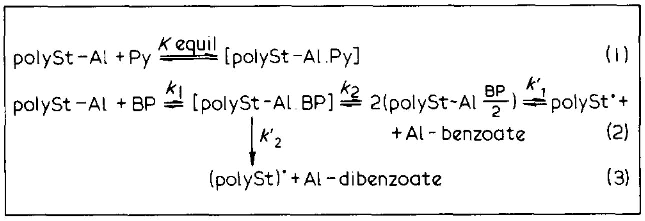
Figure 2 Constant for the polymerization rate of MMA vs. reciprocal temperature. Poly St–Al ($\bar{P}_n$ = 30)–BP–Py system, toluene was used as solvent

substituted polystyryl aluminium derivatives can also be used for the synthesis of block copolymers.

The kinetic relationships of the process and the effect of Py were investigated for the polymerization of MMA by polySt-Al–BP systems at 0°C. For a system with polySt-Al ($\bar{P}_n = 30$) the experimental dependencies of the overall polymerization rate on the concentration of the components of the initiating system and Py (*Figure 1*) are given by

$$v=k\left(\frac{[\mathrm{Al}]}{[\mathrm{Py}]}\right)^{0.5}[\mathrm{BP}]^{0.4}[\mathrm{M}]\ddagger$$

This dependence indicates that free radicals are formed as a result of the reaction of the uncomplexed form of polySt-Al with BP that occurs in exactly the same manner as in a model experiment[5]. The contribution of Py consists in decreasing the initial concentration of the organoaluminium component due to the formation of a complex and thus preventing the ineffective consumption of the initiating system (reactions 1–3).



When the equilibrium is attained rapidly, complexation (K_{equil}) is displaced to the right and the reactions with constants k_1 and k_2 are displaced to the left and the rates of the formation of free radicals are determined by reactions with the K_1 and K_2 constants, the expression of the initiation rate is obtained which is established experimentally.

Figure 2 shows the dependence of the rate constant of the process on reciprocal temperature for the system investigated. The overall activation energy is 12.8 kcal mol^{-1} and the activation energy of initiation calculated from it, E_{in}, is 16.6 kcal mol^{-1}.*

As has already been indicated[5], even low molecular weight polystyryl derivatives of Al are weaker Lewis acids than alkyl derivatives. Thus, K_{equil} for the complexation of polySt-Al ($\bar{P}_n=4$) with THF was found to be 700 ± 50 l mol^{-1} whereas K_{equil} for the reaction of $\mathrm{AlEt_3}$ with THF is 1500 ± 100 l mol^{-1} (20°, i.r. spectroscopy)[15]. It may be assumed that the increase in the length of the polystyrene chain will lead to a further decrease in the Lewis acidity of the aluminium compound. However, the determination of K_{equil} for the reaction of polySt-Al ($\bar{P}_n = 30$) with THF (i.r. spectroscopy) was impossible owing to experimental difficulties. The information found during polymerization was used to characterize the Lewis acidity of the aluminium component. The value of E_{in} itself, which for systems of this type includes the heat of complexation, i.e. E_{in} (without ED) $= E_{\mathrm{in}}$ (with ED) $+ \Delta H$, characterizes to a certain extent the complexing ability of the organoaluminium derivative**. Thus, for Al $\mathrm{Et_3}$–PB–Py it has been found to be 21.1 kcal mol^{-1} [16] as compared with the value of 16.6 kcal mol^{-1} for the polystyryl derivative of Al in this investigation. Some assumptions were made for the establishment of the order of magnitude of K_{equil} for the reaction of polySt-Al ($\bar{P}_n = 30$) with Py from these data. Assuming that E_{in} (without ED) for both Al $\mathrm{Et_3}$–BP and polySt-Al–BP systems is 1.8 kcal mol^{-1} we obtain for the polystyryl derivative the value $\Delta H = 14.8$ kcal mol^{-1}. The dependence $-RT$ ln $\mathrm{K} = \Delta H + T\Delta S$ in which ΔS was assumed to be 40.6 e.u. for both systems was used to calculate K_{equil}. For polySt-Al ($\bar{P}_n = 30$)–Py system it was found to be 1.10^3 l mol^{-1} as compared with the value of 5.10^6 for $\mathrm{AlEt_3}$–Py. Even though this calculation is tentative, the result shows that the Lewis acidity of the polystyryl derivative is much lower than that of the ethyl derivative. This is a justification of the choice of Py as an ED which was made purely empirically[5] since it is easy to show by a simple calculation that only at $K_{\mathrm{equil}} \geqslant 1.10^3$ systems of this type can be used effectively. The value of K_{equil} for other ED (ethers and esters) with $\mathrm{AlEt_3}$ is of the order of 1.10^4. Hence, for polystyryl derivatives of Al these EDs cannot ensure complexation.

Now the kinetic relationships of the MMA polymerization by systems based on polySt-Al ($\bar{P}_n = 300$, 450 and 800) will be considered. *Figure 3* shows typical kinetic curves for a system with $\bar{P}_n = 300$ when the [Py]/[Al] ratio varies from 0 to 50. In the absence of Py the rate is low in this case also and the gel effect appears fairly rapidly. *Figure 4* (*a* and *b*) shows the curves for the dependence of the rate on the [Py]/[Al] ratio for systems with $\bar{P}_n = 300$, 450 and 800. It is clear that as the length of the polymer chain bonded to aluminium increases, the rate decreases. The dependence of the rate on the [Py]/[Al] ratio may show a maximum, the latter shifting towards higher ratios with increasing value of $\bar{P}_n$. It should be recollected that at $\bar{P}_n = 30$ this dependence is an inverse proportionality and is represented by a straight line (*Figure 4b*, curve 4). The change in kinetic dependence on passing from polySt-Al at $\bar{P}_n = 30$ to derivatives of higher molecular weight probably reflects further decrease in the Lewis acidity of these compounds with increasing length of the macroradical.

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‡ The order in monomer (M) was taken to be unity

* The difference $E_p - 0.5$ Et is taken to be equal fo 4.5 kcal mol^{-1} [14]

** The mechanism of action and kinetic relationships of the $\mathrm{AlEt_3}$–BP system in the absence and the presence of ED have been reported in detail previously[16]

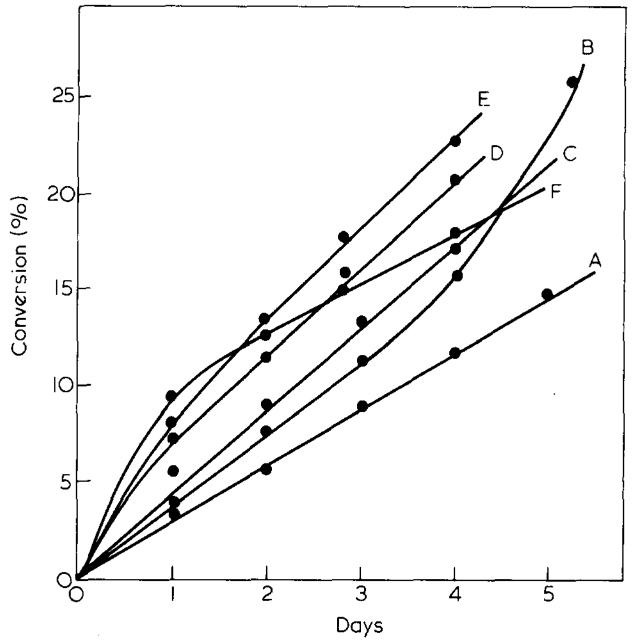

Figure 3 Typical kinetic curves in the polymerization of MMA with varying [Py]/[Al] ratio. Toluene was used as solvent, 0°C, $\bar{P}_n = 300$. Concentrations in mol l^{-1}: [Al] = $5\cdot10^{-3}$, [BP] = $4\cdot10^{-2}$, [MMA] = 6 · [Py] : [Al] = A – 50 : 1; B – without Py; C – 10 : 1; D – 3 : 1; E – 5 : 1; F – 1 : 1

The form of the dependence of the rate on the [Py]/[Al] ratio can be explained by the existence of two competing reactions occurring with the participation of an organoaluminium component: reactions with a peroxide and with an ED. As the [Py]/[Al] ratio increases the rate is determined by the reaction with peroxide before the maximum point is attained and by the ED reaction after this point. The value of the [Py]/[Al] ratio corresponding to the maximum rate depends on the Lewis acidity of the organoaluminium compound and does not depend on the concentrations of the components of the initiating system (*Figure* 4*a* and *b*). The competition of these reactions is less pronounced for polySt-Al ($\bar{P}_n = 800$). Relatively effective polymerization takes place in a system without Py. This is probably due to a considerable decrease in the rate of the reaction with BP as a result of decreasing Lewis acidity of the organoaluminium component. The introduction of Py does not markedly affect the kinetic behaviour. These results suggest the choice of conditions corresponding to the maximum kinetic effect. Apart from common concentration dependence the rate depends on the value of the high molecular weight radical (R) and, other conditions being equal, the optimum [Py]/[Al] ratio is given by the value of R.

The information obtained by using systems with PC and in the polymerization of AN is of interest because it shows the part played by the donor–acceptor reactions in which all the components of the system including the monomer take part.

Comparison of experiments 4 and 5 in *Table 2* shows that, other conditions (including temperature) being equal, the system based on PC is less active than that with BP whereas the opposite effect is observed for the system with AlR_3 (R is ethyl or isobutyl)[17]. High activity of systems based on PC was attained when the [Py]/[Al] ratio was higher than for a system with BP (*Table 2*, experiments 10 and 11). Under these conditions the polymerization is very effective even at −20°C (*Table 2*, experiment 6).*

It is easy to understand these results if it is assumed that the reaction rate of polySt-Al with PC is even higher than that with BP and, hence, it is regulated only by decreasing the initial concentration of polySt-Al and increasing the amount of Py.

Data obtained with AN are another example of the significance of the donor–acceptor reactions in these systems. AN is known to be a stronger ED than MMA

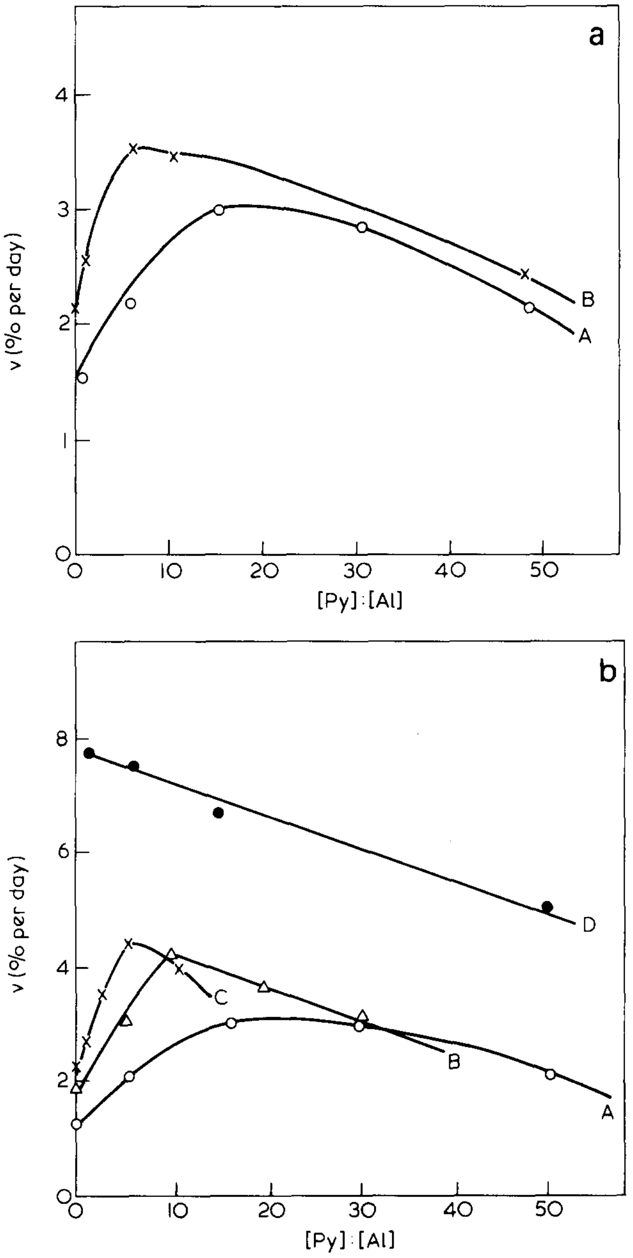

Figure 4 Polymerization rate of MMA vs. [Py]/[Al] ratio, toluene was used as solvent, 0°C, concentrations in mol l^{-1}: (a) [Al] = $2.4\cdot10^{-3}$, [BP] = $5\cdot10^{-2}$, [MMA] = 4. A – $\bar{P}_n = 800$; B – $\bar{P}_n = 300$. (b) A – [Al] = $2{,}4\cdot10^{-3}$, [BP] = $5\cdot10^{-2}$, [MMA] = 4; $\bar{P}_n = 800$; B – [Al] = $3\cdot10^{-3}$, [BP] = $4\cdot10^{-2}$, [MMA] = 4; $\bar{P}_n = 450$; C – [Al] = $5\cdot10^{-3}$, [BP] = $4\cdot10^{-2}$, [MMA] = 6; $\bar{P}_n = 300$; D – [Al] = $2\cdot10^{-2}$, [BP] = $3\cdot10^{-2}$, [MMA] = 6; $\bar{P}_n = 30$

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* [Py]/[Al] ratio of 20 was chosen more or less arbitrarily. As was shown before, the choice of an optimum ratio requires a complete kinetic investigation

Table 3 Effect of conditions of the synthesis of styrene–methylmethacrylate block copolymers on the yield and intrinsic viscosity. PolySt–Al ($\bar{P}_n$ = 300)–BP system, 0°C, toluene is used as solvent[a]

N	Molar ratio Py : Al	Contents of block copolymer fraction insoluble in acetonitrile, (wt. %)[b]	[η][c]
1	without Py	50	1.45
2	1	76	0.99
3	3	82	0.99
4	5	85	1.04
5	10	85	1.15
6	50	75	1.30

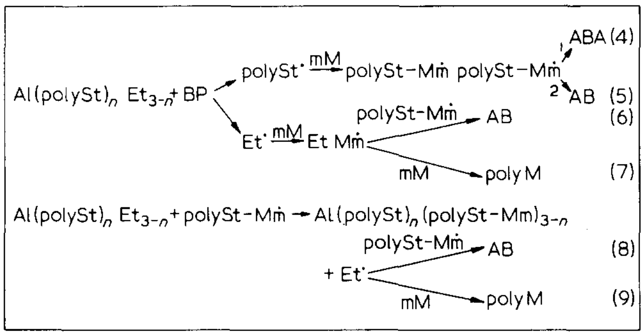
[a] Synthesized at concentrations of the components of the catalyst system and the monomer shown in *Figure 3*

[b] One fraction (15–20%) was soluble in acetonitrile and, according to g.p.c. data, is a block copolymer with a high molecular weight block of the polar monomer and low styrene contents. This fraction was not investigated

[c] Chloroform, 25°C

with respect to aluminium alkyls[17]. The possibility of carrying out an effective polymerization of AN in the absence of Py suggests that the complexing ability of AN with respect to styryl derivatives of aluminium is also higher than that of MMA and is sufficient for the prevention of ineffective interaction of catalyst components. Presumably, in this case formation of free-radicals occurs owing to the interaction of the complexed form of the organoaluminium compound with a peroxide in a manner similar to that established for systems of the type: alkylaluminium–peroxide–polar monomer[17].

The characteristics of block copolymers formed by the action of these systems were obtained for the St–MMA pair. Now we will consider the reactions leading to the formation of a block copolymer.



where A is the St block and B is the MMA block.

According to the synthesis method the polymer mixture should consist mainly of the ABA block copolymer as a result of the initiation by polySt radicals and the recombination mechanism of chain termination (reaction (4)) dominating at low temperature[18]. The formation of a two block copolymer may be related to disproportionation (reaction (5)) or to chain transfer to unsubstituted ethyl groups on polySt-Al (reaction (8)). The reaction of peroxide at unsubstituted ethyl groups could lead to the formation of homo PMMA (reactions (7) and (9)).

The information on the composition of the polymer mixture and the yield of the block copolymer was obtained for the system with polySt-Al ($\bar{P}_n = 300$)—BP (0°C). The analysis of the polymer mixture, after the unreacted homo-polySt had been removed, showed that all the polymerized MMA constitutes part of the block copolymer. As was indicated before, even for systems with polySt-Al ($\bar{P}_n = 800$) with greater amounts of unsubstituted ethyl groups, the percentage of homo-PMMA is small (*Table 2*, experiment 12). It is also suggested that the preferential formation of polystyryl rather than ethyl radicals, is related to the participation of the growing PMMA radical in chain termination. This will lead to the formation of the block copolymer of the AB type (reaction (6)).

Table 3 lists data on the effect of the conditions of the process on the yield and the characteristics of the main fraction of the block copolymer. It is clear that the change in the [Py]/[Al] ratio over a wide range does not essentially affect the yield of this fraction (about 80% of the total weight of the block copolymer). The viscosity of the block copolymer increases only slightly when the conditions are varied. These data show that the [Py]/[Al] ratio strongly influences the process kinetics without appreciably affecting the characteristics of the block copolymer. The main fraction was investigated by g.p.c. and pyrolysis chromatography. The typical shape of the chromatogram in *Figure 5* shows that the distribution of the block copolymer is bimodal: the first and the second peaks (in the direction of increasing retention volume) correspond to high and low molecular weight products, respectively.

Figure 6 shows the curves of integral *MWD* and compositional distribution according to *MW*. These data show that the high molecular polymer (log *MW* varies from 5.3 tp 6.2) constitutes the major part (*ca.* 80 wt%)* of the main fraction with styrene content of up to 20%. The information concerning its structure and that of the low molecular polymer (log *MW* varies from 4.2 to 5.3) was obtained from a combination of data on the *MW* of the

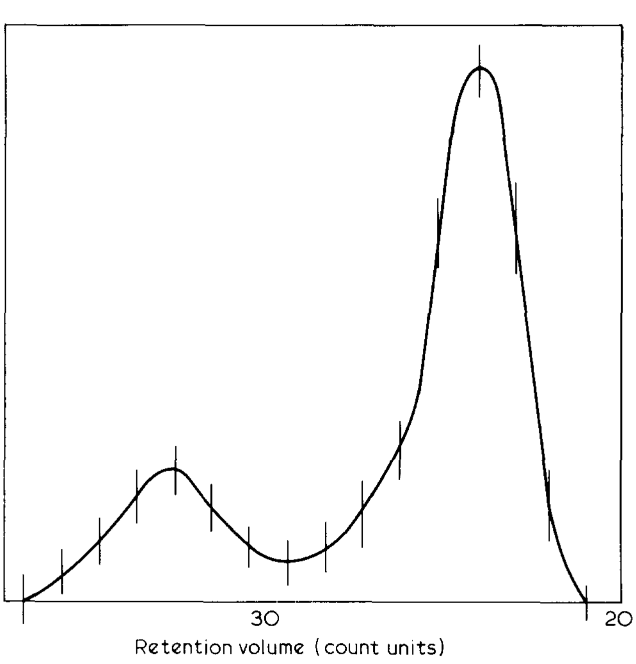


Figure 5 Typical chromatogram (g.p.c.) for the St–MMA block copolymer; toluene is used as the eluent

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* or about 70% of the total block copolymer

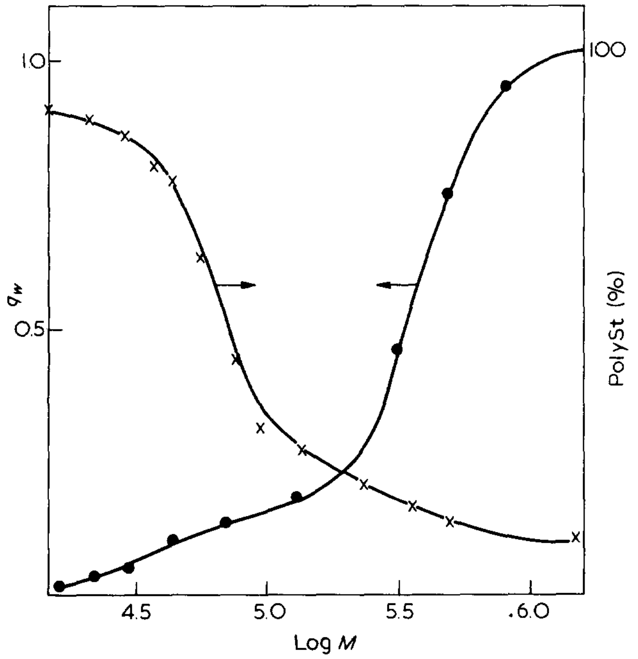

Figure 6 Curves for integral *MWD* and compositional distribution according to *MW* for St–MMA block copolymers

block copolymer, its composition (according to styrene) and the *MW* of the initial polySt. This calculation suggests that the high and low molecular weight parts of the fraction are block copolymers of the ABA and AB types, respectively.

These results show that under conditions of low temperature free-radical process systems of the polySt-Al-peroxide type make it possible to synthesize block copolymers of styrene and a polar monomer with the structure of the ABA type whereas under conditions of anionic or free-radical (polyperoxide initiators) processes copolymers with this structure cannot be synthesized.

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