

TABLE III
Comparison of Photochemical Behavior of Substituted Acrylophenones

R	$E_T(00)^a$ (kJ/mole)	Naphthalene	K_{sv}^b (liter/mole) DMHD ^c	Diphenyl
CH ₃ CO	282 ^e	381 ^f		4.4 ^d
Cl	280	260	189	48
H	292	68	42	25.5
C ₂ H ₅	282	345	161	78
CH ₃ O	277 ^e	1700 ^g		530 ^g

^a Film at liquid nitrogen temperature.

^b Benzene.

^c 2,5-Dimethyl-2,4-hexadiene.

^d Value is dependent on donor concentration.

^e Shoulder.

^f Dioxane.

^g Chlorobenzene.

from the lowest reactive $n-\pi^*$ triplet state to the nonreactive $\pi\pi^*$ state which changes the reactivity.¹⁴ Electron-withdrawing substituents preserve the $n-\pi^*$ triplet state as the spectral data indicate, but the reactivity is also decreased. Although the mechanism is not quite clear, it might include electronic and vibrational effects. It is difficult to estimate the extent of the electronic and vibrational effect of substituents on photochemical reactivity. There is a possibility of demonstrating the vibrational effect of various bulk substituents with mild electronic influence. This study is in progress in our laboratory.

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Received February 22, 1978

Revised August 7, 1978

Anionic Block Copolymerization of ϵ -Caprolactam

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Synopsis

ϵ -Caprolactam anionic homopolymerization was studied in the presence of different model activators. On the basis of the results ester- and isocyanate-terminated polymers were used as macroactivators and nylon-6-polyvinyl or polydiene block copolymers were synthesized in high yields. The physical properties and morphology of a nylon-polybutadiene triblock copolymer were characterized.

INTRODUCTION

During the last few years several reports have been published on the synthesis of lactam-based block copolymers.¹⁻⁶ Triblock copolymers with an elastomeric central sequence and terminal blocks as cohesive as nylon-6 are indeed attractive materials. The high melting point of nylon-6 (ca. 220°C) could largely improve the range of service temperature of the usual thermoplastic elastomers. On the other hand, block copolymers based on nylon might be considered in the solution of some problems of interfacial interaction between a polymeric material and nylon reinforcing fibers. Finally, the presence of hydrophobic blocks (like polybutadiene) in nylon-6 could reduce its sometimes detrimental hydrophilic character. Before these first publications appeared research in the same field had already been undertaken in our laboratories.⁷ This article aims to report the more interesting and specific results of that work.

The anionic polymerization of ϵ -caprolactam (CL) has been extensively studied.⁸ It is well known that suitable cocatalysts or activators (acid derivatives, isocyanates) which form a *N*-acyl lactam entity are needed to avoid the slow initiation observed when CL is polymerized by strong bases. Furthermore, the activator residue is incorporated at the end of the polyamide; accordingly, every polymer chain capped with one of the activators mentioned could be potentially linked to the nylon sequence.

We report here the application of this concept to ester-terminated polystyrenes (PST) and α,ω -isocyanate-terminated polybutadienes (PBD), which can be used as macromolecular activators in CL anionic polymerization.

EXPERIMENTAL

Reagents

Styrene (UCB), benzene, and cyclohexane (Baker) were dried and distilled over calcium hydride.

A solution of *sec*-butyllithium in isopentane, obtained from Metall Gesell-

schaft, was diluted with dry cyclohexane and titrated by the Gilman procedure.⁹

Ethyl chloroformate (Merck, pure) was distilled before use over tolylene diisocyanate.

Decahydronaphthalene (DHN), CL, and ethyl phenylacetate were pure reagents used without further purification. *N*-phenylcarbamoylcaprolactam and *N*-ethylphenylcarbamate were prepared according to Wiley¹⁰ and recrystallized from hexane (the melting points are 71 and 52°C, respectively). All these reagents were dried in the reactor by azeotropic distillation of benzene (final water content less than 50 ppm).

Sodium hydride (Fluka) was used as a 50% dispersion in oil.

2,4-Tolylene diisocyanate (Aldrich) was distilled at 102°C/4 mm Hg.

The α,ω -dihydroxyl polybutadiene, supplied by Phillips Petroleum Co. (Butarez HTS), had the following properties: $\bar{M}_n = 4400$; hydroxyl = 0.7%; unsaturation: vinyl/cis/trans = 26/37/37.

Synthesis of Ester-Terminated Polystyrene

In a previously flamed, nitrogen-purged, 1-liter flask were added 600 ml of dry benzene and 22 ml of *sec*-butyllithium molar solution. After cooling in an ice bath 240 ml of dry styrene was also added and the reaction was then allowed to proceed for 10 hr. The living polystyryllithium was dropped through a stainless steel capillary into 30 ml of stirred ethyl chloroformate. After reaction the solution was precipitated twice into methanol; the final product was filtered and dried under vacuum.

CL Polymerization by Model Activators

To start the procedure 20 g of CL, 100 ml of DHN, 200 ml of benzene, and 2×10^{-3} mole of activator were stirred in a nitrogen-purged, 1-liter glass reactor. After complete benzene distillation the temperature was increased and stabilized at 200°C; 100 or 400 mg of sodium hydride dispersion was then added and stirred under a nitrogen flow. The product obtained was washed with hexane, dissolved in 100 ml of concentrated formic acid, and precipitated into acetone. The resulting powder was filtered, the unreacted CL extracted by methanol in a Soxhlet apparatus, and the polyamide dried under vacuum.

Synthesis of Diblock Polystyrene-Nylon-6 Copolymers

The procedure was the same as in CL homopolymerization, but with ester-terminated polystyrene as the activator. After 2 hr at 200°C the apparatus was allowed to cool. The crude polymeric product was washed with hexane, dissolved in formic acid, and reprecipitated into methanol. The unreacted CL was eliminated by extraction with methanol and the homopolystyrene was removed by extraction with butanone.

Synthesis of Triblock Nylon-6-PBD Copolymers

As a preliminary 36 g of Butarez HTS (9×10^{-3} mole), 350 ml of benzene, and eventually a suitable amount of DHN were introduced into a nitrogen-purged, 1-liter glass reactor. Benzene was distilled off, 10^{-2} mole of TDI in 40 ml of dry benzene were added, and the whole solution refluxed for 12 hr. After the addition of 80 g of dry CL the benzene was completely removed, the temperature fixed at 105°C, and 180-mg of NaH introduced and stirred under a nitrogen flow. After 16 hr of reaction time the solid material obtained was dispersed in formic acid (500 ml) and poured into methanol as described by Yamashita et al.¹ The precipitated polymers were filtered and washed with the precipitant. After drying *in vacuo* the polymer was extracted with hexane in a Soxhlet apparatus to isolate the polybutadiene homopolymer as the hexane-soluble part.

Analysis

The composition of nylon-6-based block copolymers was established by elementary analysis, and the molecular weights were measured in *m*-cresol at 70°C with a Hewlett-Packard 502 osmometer equipped with a Schleicher and Schuell 0-8 membrane. Intrinsic viscosities were determined in *m*-cresol at 25°C.

The unblocked nylon-6 content was evaluated by extraction with trifluoroethanol (TFE). This was accomplished by stirring the hydrocarbon-extracted copolymer with TFE, followed by centrifugation, decantation, and removal of solvent by distillation under reduced pressure.

The polydispersity of the polymeric samples was analyzed by gel permeation chromatography (GPC), in tetrahydrofuran (THF) at 30°C for polystyrene and in hexamethylphosphotriamide at 105°C for nylon-6. The content of coupled polystyrene after chloroformate deactivation was evaluated from GPC peak surfaces integration by a DuPont curve resolver. The Styragel columns used were calibrated with polystyrene standard samples; the polydispersity indexes calculated by this method for nylon-6 and block copolymers have essentially a comparative meaning.

A DuPont 990 thermal analyzer was used to detect the mean transitions in the block copolymers; it was equipped with a DSC cell (heating rate: 20°C/min) or a TMA device (5°C/min) which can be used in expansion (sample loading: 2 g, 0.01 in. thick) or in extension mode (films $\frac{5}{8}$ in. long).

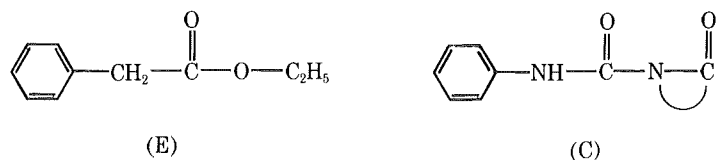
Ultramicrotome sections or thin films of PBD-nylon-6 copolymers [(6-7) $\times 10^2$ Å] were observed by transmission electron microscopy. The PBD phases can be stained by exposure to osmium tetroxide (OsO₄) vapors (24 hr); if not, the crystalline domains appear as the darkest ones. The thin films were prepared from 0.5% *m*-cresol/chloroform (1/1) solutions obtained by a 4 hr refluxing of the solvent; a glass plate was introduced in the solution (1 min) and then slowly drawn out. The molding of the PBD-nylon-6 block copolymer was performed at 280°C for 2 min and followed by fast cooling. About 1% of cyanox SS 2.2'-methylene-bis(4-methyl-6 *tert*-butyl phenol) was added as antioxidant to the copolymer; an eventual crosslinking of the molded samples has not been ascertained by repressing.

RESULTS AND DISCUSSION

CL Anionic Polymerization in the Presence of an Ester-Terminated Polymer

Optimization of CL Anionic Polymerization with Model Compounds

The CL polymerization was studied in DHN at 200°C with an identical amount of reagents, except for the molar ratio of base catalyst over activator $[S]/[A]$. Two different activators were used: ethylphenylacetate (E) as an ester model, and *N*-phenylcarbamoylcaprolactam (C) as a model for the *N*-acyl lactam propagating species:



The results are summarized in Table I where (conversion/ \bar{M}_n) represents the conversion over mean number-average molecular weight ratio. How can this ratio vary during polymerization? It will remain unchanged as long as the total number of growing chains is constant, despite an eventual redistribution of chain lengths. It will increase when new chains are formed: spontaneously (very slow

TABLE I
Anionic Polymerization of ϵ -Caprolactam: Influence of the Nature of the Activator and of the Lactam Salt/Activator Molar Ratio ($[S]/[A]$)^a

Activator ^b	$[S]/[A]$	Time (min)	Conversion ^c (%)	Conversion			Polydispersion index
				\bar{M}_n^d	\bar{M}_n ($\times 10^6$)	$[\eta]^e$ (dl g ⁻¹)	
C	1	5	66	13,500	48.9	0.98	3.3
		10	75	15,500	48.4	1.31	
		30	94	20,000	47.0	1.50	
		120	96	20,500	46.8	1.61	
C	4	5	69	17,500	39.5	1.37	2.9
		30	63	12,500	50.4	0.68	
		120	86	11,500	74.8	0.64	
E	1	5	10	12,000	8.3	0.86	3.1
		10	21	14,500	14.5	0.96	
		15	38	20,500	18.5	1.10	
		30	67	21,000	31.9	1.80	
		120	89	22,000	40.5	1.74	
E	4	5	62	13,500	46.0	0.72	3.6
		120	43	10,000	43.0	0.76	

^a Conditions: 200°C, $[CL] = 1.5M$ in DHN, $[CL]/[A] = 88$.

^b C corresponds to *N*-phenylcarbamoylcaprolactam and E to ethylphenylacetate.

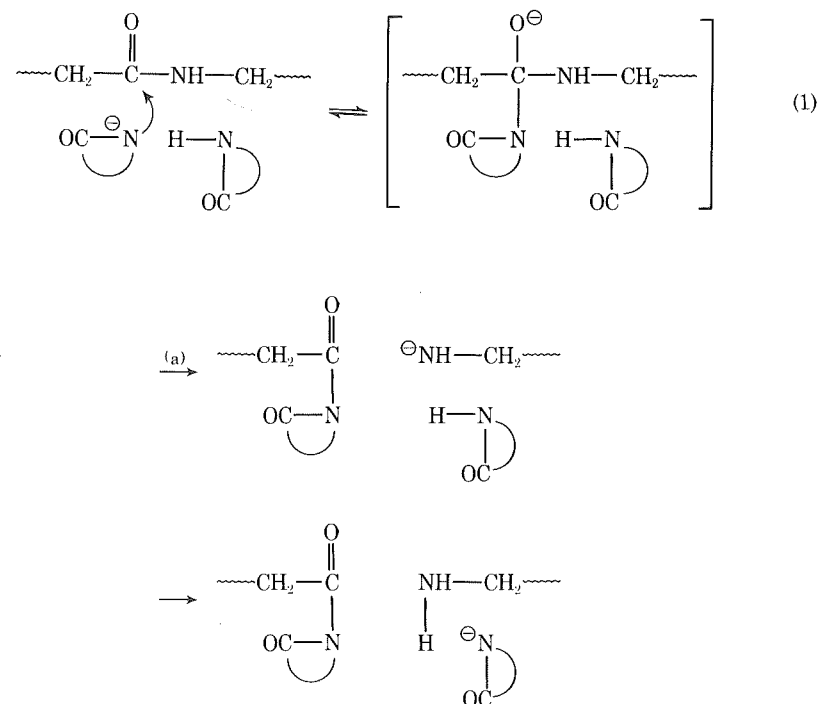
^c Evaluated after precipitation and extraction of the polymer with methanol.

^d Osmometry in *m*-cresol.

^e In *m*-cresol at 25°C.

initiation) by transfer of active centers, or by chain rupture. On the contrary, if chains are linked together (e.g., by grafting), this ratio will decrease.

With the C-type activator and an ($[S]/[A]$) ratio of 1, an almost constant value of the (conversion/ \bar{M}_n) ratio, and accordingly the number of growing chains, is observed beyond 66% conversion. When the $[S]/[A] = 4$, a large increase in the (conversion/ \bar{M}_n) ratio and a decrease in \bar{M}_n are noted, which could be attributed to a nucleophilic attack on the polyamide chain [eq. (1)] which involves the formation of an alkoxide intermediate; its evolution according to path (a), although not highly probable, could, however, be observed at increasing anionic concentration. This occurrence of path (a) could be explained by the "scavenging" of the stronger leaving group $^{\ominus}NH-CH_2$ by a CL molecule solvating the reaction site:



If low-molecular-weight oligomers are extracted by methanol, the values of (conversion/ \bar{M}_n) will be too low, but the error relating to conversion and \bar{M}_n will decrease as these parameters increase. Consequently the trend observed for the variation of (conversion/ \bar{M}_n) could be more pronounced for $[S]/[A] = 4$, whereas the decrease assumed as not significant for $[S]/[A] = 1$ could perhaps be considered and means the possible occurrence of a grafting process.

Moreover, with the C-type activator and a $[S]/[A]$ ratio of 1, the \bar{M}_n at total conversion is nearly twice its theoretical value ($[CL]/[A] = 88$). In other words, half the activator molecules must disappear at the beginning of the polymerization, possibly by a Claisen-type condensation between low-molecular-weight growing chains and/or initiating species [eq. (2)].

It should be noted that Sebenda⁸ has also confirmed the drastic change in the

controlling the anionic polymerization of CL are given extensive coverage in the scientific literature.^{8,13}

CL Block Copolymerization with an Ester-Ended Macroactivator

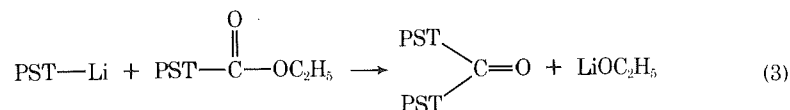
From the foregoing results the following conclusions can be drawn about CL block copolymerization:

(1) Claisen-type condensation is responsible for the disappearance of a large number of growing entities. In block copolymerization, however, the growing centers are at the ends of longer chains: the greater their length, the lower the mobility, accessibility, and probability of meeting these entities. In other words, the homopolymerization tests described above are an extreme case, and the efficiency of CL block copolymerization is not necessarily hampered by side-reactions.

(2) To avoid a nucleophilic attack [eq. (1)] of the polyamide sequence the ([S]/[A]) ratio is kept at 1.

(3) The molecular weight distribution of nylon-6 is not obviously affected by the slow initiation step characteristic of the ester activator. An ester-ended polymer can thus be used as an activator in CL block copolymerization. Polystyrene (PST) has been chosen.

As described in the Experimental section, ester-ended PST is prepared by deactivation of polystyryl-lithium into an excess of ethyl chloroformate. A secondary coupling reaction can take place, however [eq. (3)]:



In benzene and even in an excess of chloroformate at least 20% coupling is observed. This fact could be ascribed in part to the association of living PST-Li chains in benzene.

Block copolymerization was performed under the conditions provided for the homopolymerization tests; however, variable amounts of diluent (DHN) were used. After polymerization the crude product obtained was extracted successively with two different solvents: methanol, which is a selective solvent of the unreacted CL and low oligomers eventually present, and butanone, a selective solvent of PST. The different fractions were weighed and analyzed as indicated in Table II.

An important amount of PST seems to remain unreacted, even when, in the absence of diluent, the conversion of CL is complete (exp. 4). In the latter case the IR spectrum of the butanone-soluble fraction shows no absorption characteristic of the carbonyl group of nylon; the extracted PST is thus probably inactive and represents about 30% of the initial amount of PST. On this basis the percentage of PST incorporated in the block copolymer has been recalculated (footnote c, Table II); its variation with the dilution is irregular.

The nylon content in the copolymer was evaluated by elemental analysis and also by calculation, assuming that no PST was extracted by methanol. For experiments 2-4 the results are in good agreement (Table II), which favors the absence of oligomeric and methanol-soluble nylon sequences. That is not the case for experiment 1 characterized by a lower CL over PST ratio. In the last column of Table II the copolymerization yield has been calculated; it is increasing

TABLE II
Polystyrene-Nylon-6 Diblock Copolymers Obtained from Ester-Terminated Polystyrene^a

Exp. No.	Mono- mer (CL) (g)	Solvent (DHN) (ml)	Methanol- soluble fraction (g)	Methanol-insoluble fraction						
				Butanone-soluble fraction		Butanone-insoluble fraction		% copoly- meriza- tion ^e		
				% PST g	% PST used ^b	% PST used ^c	% NY-6 g	% NY-6 calc ^d	% NY-6 meas.	
1	10	40	3	11	31	45	12	58	65	57
2	30	200	28	8	50	73	10	20	18	25
3	30	40	3	11	31	45	32	84	83	78
4	30	0	0	5	69	100	41 ^f	73	72	100

^a Conditions: 2 hr in DHN at 200°C, 16 g of PST ($\bar{M}_n = 10^4$).

^b Percentage of PST incorporated in block copolymer, assuming 16 g of active PST.

^c Same as b assuming 5 g of inactive PST.

^d Calculated by assuming that no PST is present in the methanol-soluble fraction.

^e Weight of copolymer obtained, divided by the weight of monomer plus active PST (11 g).

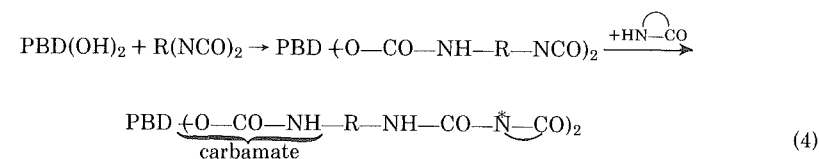
^f $\bar{M}_n = 30,000$.

with the concentration of the medium, and the CL over macroactivator ratio (exps. 1 and 3).

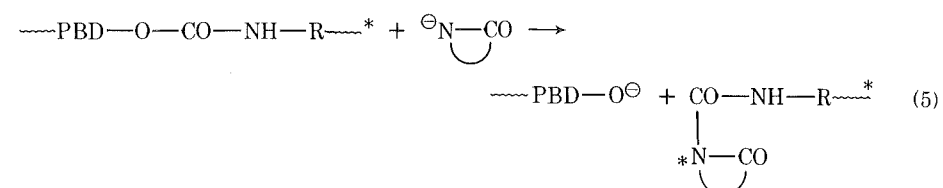
Caprolactam Anionic Polymerization in the Presence of an α,ω -Isocyanate-Terminated Difunctional Polybutadiene

Synthesis of Nylon-6-Polybutadiene-Nylon-6 Triblock Copolymer

Isocyanate-ended polymers should be excellent macroactivators of CL polymerization because they form a *N*-acyl lactam function by adding a CL unit. In an attempt to prepare thermoplastic elastomers based on nylon-6 a commercial dihydroxyl polybutadiene ($\bar{M}_n = 4400$) has been treated with a suitable amount of tolylene diisocyanate to ensure simultaneous chain extension and isocyanate functionalization. As shown by eq. (4), however, a carbamate group is also formed:

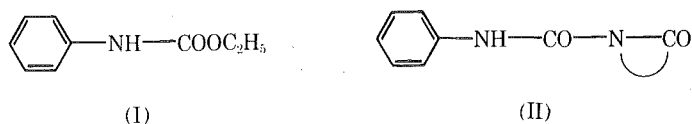


This group can be attacked by a lactam salt with the release of PBD and growth of a homopolyamide chain [eq. (5)]:



To obtain the required triblock copolymer in high yield and purity it is necessary to limit this nucleophilic attack on the carbamate but to extend it on the *N*-acyl lactam end group (propagation). To study this problem the *N*-ethyl phenyl-

carbamate (I) and the previously mentioned *N*-phenyl-carbamoyl caprolactam (II) were synthesized:



The efficiency of these two compounds as activators in CL homopolymerization has been compared at different temperatures and in the absence of solvent; Figure 3 clearly indicates that 105°C is an interesting temperature. In fact, CL is polymerized to the highest conversion (86%) by *N*-acyl lactam (II) at 105°C, whereas under these conditions the carbamate initiator (I) ensures only 10% conversion. Furthermore, it has been shown that tolylene diisocyanate/CL adduct decomposes between 108 and 125°C (ref. 14). Thus the carbamate cleavage reaction does not compete significantly with the propagation step, and these experimental conditions can be applied to CL polymerization by the isocyanate-terminated PBD. This conclusion has been supported in an article⁵ that mentions higher yield and molecular weight at 105°C for similar experiments.

Table III summarizes the results obtained with an extended PBD ($\bar{M}_n = 20,000$) capped with isocyanate functions; although the time parameter has not been critically evaluated, the deleterious influence of a diluent is again clearly placed in evidence.

In fact, an increasing dilution is responsible for a significant decrease in CL conversion, nylon block length, and copolymerization efficiency. As already discussed, the comparison between calculated and experimental contents in nylon-6 in the copolymer, except for the highest dilution (exp. 3), indicates the absence of short-length nylon sequences (i.e., hexane-soluble copolymer).

Without diluent the copolymerization yield is high (87%) and \bar{M}_n (50,000) is only a little lower than the theoretical value based on a monomer/catalyst molar ratio (60,000). This difference may possibly be attributed to the nucleophilic attack of the carbamate groups; when these groups are inside the PBD extended chain, a triblock with a shorter central sequence and a diblock copolymer are formed simultaneously whereas the attack of one of the terminal carbamate groups leads to a diblock and polyamide chain. Because the average proportion of internal carbamate links is higher (four times), the decrease in \bar{M}_n must be

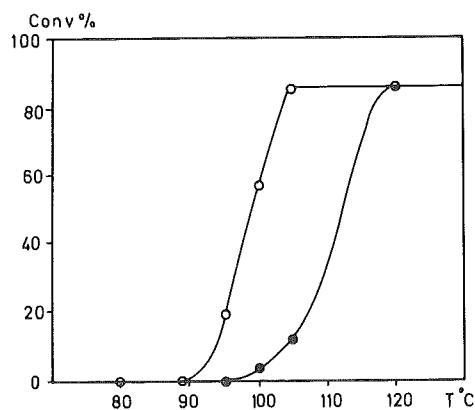


Fig. 3. Anionic polymerization of ϵ -caprolactam at different temperatures: (○) carbamate activator, (●) acyl lactam activator.

TABLE III
Polybutadiene-Nylon-6 Block Copolymers^a

Exp. No.	Solvent (DHN) (ml)	Hexane-soluble fraction (g)	Hexane-insoluble fraction					
			Weight (g)	$[\eta]^c$ (dl g ⁻¹)	% NY-6 (calc) ^e	% NY-6 (elementary analysis)	NY-6 yield ^f (%)	Copolymerization yield ^g (%)
1	—	5 ^b	96	2.9 ^d	68	67	80	87
2	200	6	51	0.2	41	40	25	46
3	500	19	29	0.06	41	36	13	26

^a Conditions: 36 g of extended Butarez HTS ($\bar{M}_n = 20,000$), 80 g of CL, 3.6 mM of NaH and 2 mM of bis(dimethylamino)hexane, 16 hr at 105°C.

^b No carbonyl absorption in the IR spectrum (inactive Butarez).

^c In *m*-cresol at 25°C.

^d $\bar{M}_n = 50,000$.

^e $1 - [(36 \text{ Hexane-soluble fraction of weight}) / \text{hexane-insoluble fraction of weight}]$.

^f Weight of NY-6 in copolymer/80 g of CL.

^g Hexane-insoluble fraction of weight/(80 g of CL + 31 g of active Butarez).

attributed principally to the formation of diblock and shorter triblock copolymers. The percentage of homopolyamide determined by three extractions with trifluoroethanol is indeed rather low (18%) and in agreement with the results published for diblock copolymers from isocyanate-terminated polybutadiene or polystyrene.³ This value can be attributed to a partial contribution of the carbamate to the initiation of the lactam polymerization as well as to some cleavage reactions described by Sebenda⁸ as secondary reactions. The copolymer (hexane-insoluble fraction) contains 33% of PBD ($\bar{M}_n = 20,000$) and 67% of nylon-6, the length of which depends on the structure of the copolymer obtained. It is difficult, however, to establish the relative percentages of the different macromolecular species really present (triblocks and diblocks especially) and to evaluate the mean length of the nylon sequences.

Some physical characteristics of this nylon-6-based copolymer are given below.

Physical Properties of a Nylon-6-PBD Block Copolymer

Thermal (DSC) and thermomechanical (TMA) analyses made the heterophase character of the copolymer clearly evident. The glass transition of polybutadiene is observed at -70°C for both homo- and block copolymers. The melting temperature (T_m) of nylon-6 is clearly apparent around 215–220°C, whatever the sample preparation: powder, molded, or solvent-cast film. The phase separation observed below nylon's T_m does not seem to disappear even at temperatures well above this upper transition. In fact, the copolymer is difficult to process by compression molding because of its high melt viscosity and elasticity. The melt-flow index measured at 240°C under 12.5 kg is 0.9 g/10 min and increases with time. Furthermore, compression molding at 280°C induces an orientation effect in the copolymer observed by polarized light microscopy; an annealing at 230°C (10°C above T_m) has almost no influence on this characteristic. Such behavior is believed to be related to the retention of a physical network well above the nylon melting temperature.

The molded, and thus oriented, sample analyzed by TMA exhibits another transition at 40°C (along the orientation direction) or at 100°C (in the perpen-

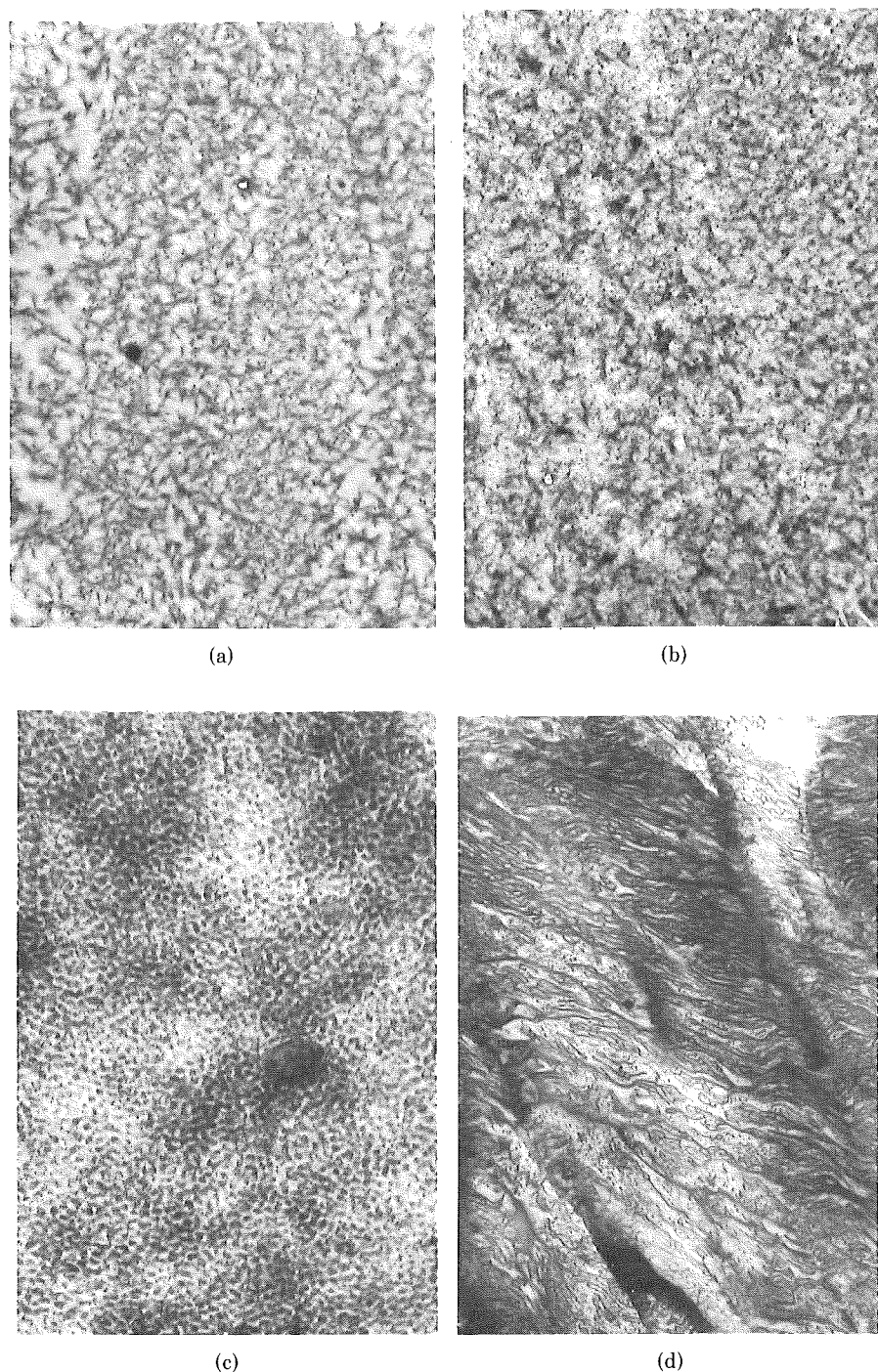


Fig. 4. Electron photomicrographs of a nylon-6-polybutadiene triblock copolymer: (a) solvent-cast film, unstained ($\times 10^4$), (b) solvent-cast film, O_8O_4 stained ($\times 10^4$), (c) solvent-cast film, O_8O_4 stained ($\times 10^5$), (d) ultramicrotomed film from a hot compression-molded sample, O_8O_4 stained ($\times 5 \times 10^4$).

dicular direction). This observation is a good illustration of the anisotropic character of the molded copolymer.

These first morphological features are confirmed by electron photomicrographs obtained from a solvent-cast film observed by transmission at two different magnifications [Fig. 4(a) and (b), $\times 10^4$ and (c), $\times 10^5$]. The micrographs (a) and (b) correspond to the sample stained with O_8O_4 (b) or unstained (a). In micrograph (a) the crystalline entities are easily observable (dark domains), whereas when stained [micrograph (b)] the PBD domains become apparent, especially at the periphery of the nylon crystallites. Micrograph (c), obtained with a higher resolution, demonstrates that the dark PBD domains are really small ($\approx 100 \text{ \AA}$) and rather regularly distributed in a continuous nylon matrix; despite the high incompatibility between PBD and nylon-6, the phase separation is developed at a fine microscopic level. If the block copolymer is hot-compression molded and then quickly cooled [Fig. 4(d), $\times 5 \times 10^4$], its morphology is deeply modified and characterized by a pronounced orientation effect and the coalescence of the PBD domains. The retention of a two-phase system at a high processing temperature is evident and must be correlated to the large difference (5.4) between the solubility parameters of each sequence.¹⁵

The tensile strength and elongation at break have also been measured on a molded and solvent-cast sample and compared with the corresponding values published for the same composition of PBD-nylon-6 diblock copolymer crosslinked with dicumyl peroxide⁴ (Table IV).

The values of the tensile strength and elongation at break are similar to those of pure nylon-6 and actually not to that of an elastomer, in agreement with the photomicrographs [Fig. 4(c)] in which PBD is the discontinuous phase.

Obviously the molding of the triblock copolymer at high temperature is responsible for the degradation reactions and lowering of its mechanical properties. This is in accordance with the time dependence of the melt flow index. In the absence of these degradation effects the triblock copolymer presents mechanical properties similar to those of the corresponding crosslinked diblock copolymer. It must be mentioned that the latter can be processed at room temperature. Such easy workability has been attributed to the copolymer synthesis that takes place in a selective solvent of PBD and so favors the development of a continuous flexible phase.³ In regard to processability Allen and Eaves⁶ emphasize the importance of the nature of the diisocyanate used in the macroactivator preparation. In contrast to an aromatic diisocyanate the aliphatic favors lower values of the melt flow index of the corresponding injection-molded (230°C) copolymers; thus the thermal stability of the urethane linkage formed is important.

TABLE IV
Mechanical Properties of Polybutadiene-Nylon-6 Block Copolymers

	Tensile strength (MPa)	Elongation at break (%)
Triblock copolymer molded film	22.5	80
Triblock copolymer solvent-cast film	39.2	130
Crosslinked diblock copolymer ^a	31.9	135

^a Reference 4.

CONCLUSIONS

Ester- and isocyanate-terminated polymers are effective activators in the anionic polymerization of CL.

Preliminary studies with different model activators indicate that the polydispersity of the polyamides obtained is not directly related to the initiation rate; this suggests the existence of redistribution processes. However, the more active the activator, the milder the synthesis conditions can be. Other secondary reactions can be avoided by the use of a lactam salt/activator molar ratio of one.

The use of macromolecular activators apparently permits the limitation of the Claisen-type condensation responsible for the disappearance of growing entities at the beginning of CL homopolymerizations. The incorporation of the macroactivator in the block copolymer formed will be dependent only on its functionality and, like the CL conversion, on the presence of a diluent. In the absence of the latter the yield in block copolymer amounts to 90% or higher.

If isocyanate-terminated polybutadiene that contains carbamate groupings in its chain is used, special attention must be paid to limit the nucleophilic attack of these groups: 105°C seems to be the optimum polymerization temperature.

PBD-nylon-6 block copolymers (33% PBD) present a heterophase character, even above the nylon-6 melting temperature. In the molten state they are easily oriented and their properties become anisotropic. Electron photomicrographs confirm these results, and the mechanical properties are sensitive to the thermal history of the samples.

These results have been extended to other lactams (e.g., nylon-12 block copolymers) and to other OH-terminated blocks; in particular, polyethyleneglycols ($\bar{M}_n = 20,000$) which promote a high rate of CL polymerization.

The authors would like to thank Dr. H. L. Hsieh (Phillips Petroleum Co.) for supplying a sample of Butarez HTS and Mr. A. Lecloux and G. Gobillon (Solvay Co., Brussels) for the electron photomicrographs. One of the authors (D.P.) is indebted to I.R.S.I.A. (Brussels) for a fellowship.

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Received February 28, 1978

Revised August 7, 1978

Anionic Copolymerization of Optically Active α -Methylbenzyl Methacrylate and Trityl Methacrylate. I. Reactivity of Monomers

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Synopsis

The monomer reactivity ratios were determined in the anionic copolymerization of (S)- or (RS)- α -methylbenzyl methacrylate (MBMA) and trityl methacrylate (TrMA) with butyllithium at -78°C , and the stereoregularity of the yielded copolymer was investigated. In the copolymerization of (S)-MBMA (M_1) and TrMA (M_2) in toluene the monomer reactivity ratios were $r_1 = 8.55$ and $r_2 = 0.005$. On the other hand, those in the copolymerization of (RS)-MBMA with TrMA were $r_1 = 4.30$ and $r_2 = 0.03$. The copolymer of (S)-MBMA and TrMA prepared in toluene was a mixture of two types of copolymer: one consisted mainly of the (S)-MBMA unit and was highly isotactic and the other contained both monomers copiously. The same monomer reactivity ratios, $r_1 = 0.39$ and $r_2 = 0.33$, were obtained in the copolymerizations of the (S)-MBMA-TrMA and (RS)-MBMA-TrMA systems in tetrahydrofuran (THF). The microstructures of poly[(S)-MBMA-co-TrMA] and poly[(RS)-MBMA-co-TrMA] produced in THF were similar where the isotacticity increased with an increase in the content of the TrMA unit.

INTRODUCTION

A number of articles have been published on the optically active vinyl copolymers in which the unit from nonchiral monomer contributes to the chiroptical properties of the copolymer.¹⁻¹¹ In such contributions the steric interaction between the component comonomers and the microstructure of the polymer may play an important role.

The isotacticity of the poly[(RS)-MBMA] obtained with butyllithium (BuLi) in toluene at -78°C is considerably lower than that of the poly[(R)-MBMA] prepared under the same conditions.¹² This indicates that the stereocontrol in the polymerization is greatly affected by the configuration of the substituent ester group. On the other hand, trityl methacrylate (TrMA) produces a highly isotactic polymer with BuLi in tetrahydrofuran (THF), as well as in toluene, because the bulky trityl group prevents syndiotactic placement. The trityl group forces the isotactic chain of the polymer to take a rigid conformation that is assumed to be helical by inspecting a molecular model.^{13,14} Consequently, if a copolymer of TrMA and an optically active monomer contains an isotactic sequence of the TrMA units, it may be expected that the sequence will take a helical conformation in one screw under the influence of the chirality of the comonomer. In an earlier article we reported briefly that the copolymer of TrMA with a small amount of (S)-MBMA showed abnormal chiroptical properties that were considered attributable to a one-handed helix in the isotactic TrMA sequence.¹⁵

The present work was done to obtain the basic information on the anionic