

Particulate Rubber Modified Nylon 6 RIM

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Synopsis

Nylon 6 produced by the reaction injection molding (RIM) process is toughened through block copolymerization of caprolactam with functional, rubbery prepolymers. This article describes an alternate route, where caprolactam is polymerized in the presence of a dispersed particulate rubber. The particulate rubber employed in this study has a core-shell morphology with a soft, crosslinked butadiene-based rubbery core and a grafted styrene-acrylonitrile shell. The core-shell rubber is dispersed as a latex in caprolactam to high quality dispersions which, on anionic polymerization, give tough castings. Incorporation of a reactive monomer such as hydroxypropyl methacrylate in the graft shell brings about further improvement in impact strength.

INTRODUCTION

Nylons are generally regarded as "tough thermoplastics" since they exhibit good elongation and high energy to break. However, they are notch sensitive; i.e., they are not resistant to crack propagation, and this often results in brittle or catastrophic failure. Incorporation of a suitable elastomer as a dispersed phase helps overcome this deficiency, and this has been amply demonstrated in the literature.¹⁻⁵ Such elastomers are normally dispersed in nylons by melt blending under high shear, and the polymers so toughened exhibit ductile failure and a greatly reduced notch sensitivity.

In the case of nylon 6 polymers prepared by the reaction injection molding (RIM) process, where caprolactam monomer is polymerized in a mold, the process dictates that any modification to improve its impact strength be carried out during polymerization. Presently, the nylon 6 RIM products are toughened by block copolymerizing caprolactam with low molecular weight polyethers⁶ or polybutadienes⁷ with terminal functional groups.

An alternate route to toughen nylon 6 RIM is believed to be through particulate rubber of modification. The objectives of this investigation are to determine if graft rubbers of core-shell morphology and finite particle size can be effectively dispersed in caprolactam and whether such dispersions can be polymerized to a nylon 6 RIM with improved impact properties.

EXPERIMENTAL

The particulate rubbers employed in this study were prepared by emulsion graft polymerization.

The rubber latex used here was of a butadiene-acrylonitrile (93/7) copolymer, polymerized at 75°C to high conversion.⁸⁻¹⁰ The rubber particle size is about 0.2 μm , and the latex solid content was about 45%.

Graft polymerization of monomers to form the thermoplastic shell was carried out by the procedure described by Baer.³ In the case where the latex

TABLE I
Compositions of Various Graft Latexes

Graft latex no.	Core : shell (wt ratio)	Shell composition (S/AN/X)
A	100 : 25	70/30/0
B	100 : 25	90/10/0
C	100 : 25	100/0/0
D	100 : 40	70/30/0
E	100 : 60	70/30/0
F	100 : 25	60/30/10 HPMA ^a

^aHPMA = 2-hydroxypropyl methacrylate.

was coagulated, the rubber was stabilized with 2% Polygard and 1% Ionol based on the weight of polybutadiene in the graft latex. The stabilized latex was coagulated in a hot (95–98°C), 3% solution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in water. The coagulated material was filtered, washed several times with water, and dried in a vacuum oven at 60°C.

Compositions of the various graft rubbers employed in this investigation are listed in Table I.

Preparation of Graft Rubber Dispersion in Caprolactam

Caprolactam (containing 0.5% Flectol-H stabilizer) as an 80% solution in water was charged to a four-necked round bottom flask fitted with a mechanical stirrer, thermometer with a temperature controller, a nitrogen inlet, and a distillation head. Graft latex was then slowly added at room temperature with good agitation. The contents in the flask were gradually heated to about 90–100°C with a good nitrogen sweep to strip off water. When all the water was stripped off, isophthaloyl bislactam initiator was added, and the temperature was raised to 130°C. Some caprolactam was distilled over, under vacuum, to obtain a dry dispersion suitable for subsequent anionic polymerization. A typical recipe used for the preparation of a dispersion is given in Table II.

Polymerization of Dispersion in Mold

Graft rubber dispersion in caprolactam was mixed with an appropriate amount of a Grignard catalyst, caprolactam magnesium bromide, and trans-

TABLE II
A Typical Recipe for Particulate Rubber Dispersion in Caprolactam

80% Aqueous caprolactam solution (with 0.5% Flectol H):	1116 g
Graft latex ^a :	552 g
1. Strip off all water	
Isophthaloyl biscaprolactam:	8.67 g
2. Strip 40 mL caprolactam	
Recovered dispersion: 1000 g	
% Core-shell rubber in dispersion:	17.0
% Rubbery core in dispersion:	14.0
Isophthaloyl biscaprolactam concn:	3.2 m mol/mol caprolactam

^aCore: 93 Bd/7 AN, 0.17 μm . Shell: 70 S/30 AN, 25 phr. % Total solids of latex: 31.8.

TABLE III
A Typical Recipe for Polymerization of Particulate Rubber Dispersion

Reservoir A (dispersion with Initiator)	Reservoir B (catalyst)
Core-shell rubber Dispersion: 600 g	300 ml 0.6 M Caprolactam magnesium bromide solution in caprolactam
Ratio of pump speeds: A/B = 6:1	
Mold thickness: 1/8 in.	
Mold temperature: 160°C	
Peak temperature: 172°C	
Time to peak: 240 s	
Initiator (isophthaloylbiscaprolactam): 3.0 mmol/mol caprolactam	
Catalyst (caprolactam magnesium bromide):	13.5 mmol/mol caprolactam
% Rubbery core in final casting:	12.0

ferred to the mold. A pump-casting setup similar to that employed by Gabbert et al.⁷ was assembled and used. Dispersions at 120–130°C were transferred to one of the reservoirs of the RIM machine, and the caprolactam magnesium bromide catalyst to the other, and the two were pumped through a series of static mixers into the mold. The Zenith gear pumps used for this purpose were preheated in an oven at 130°C, and the transfer lines were electrically heated to prevent the caprolactam monomer from solidifying. The ratio of the dispersion to catalyst was adjusted by setting the two pumps at appropriate speeds.

Polymerization was generally carried out at a mold temperature of 160°C, and the casting was held in the mold for about 15 min. The peak temperatures of the exotherms were normally achieved in less than 5 min. A typical polymerization recipe is given in Table III.

Microscopy. Electron microscopic studies were carried out on a JEOL 100U transmission electron microscope and an ISI DS-130 scanning electron microscope. Specimens for transmission electron microscopy were stained in a 1% aqueous OsO₄ solution for 96 h and then washed in water for 24 h. 1000Å thick sections were cut from the hardened block using a glass knife on a Sorvall MT-2B ultra microtome at room temperature. Specimens for scanning electron microscopy were prepared by coating the fractured surface first with carbon and then with a 150 Å thick coating of gold in a sputter coater.

Testing. ASTM procedures were used to determine the tensile and flexural properties as well as the Izod impact. Notched (0.01 in. radius) bars (5 × 1/2 × 1/8 in.) were used for impact tests. Properties reported are on dry as-molded specimens.

RESULTS AND DISCUSSION

The goal of this project is to upgrade the toughness of nylon 6 RIM through particulate rubber modification. For maximum enhancement of

toughness, it is desirable that the following conditions be satisfied:

- The rubber graft should be colloiddally dispersible in caprolactam monomer.
- Such a dispersion should be stable during caprolactam polymerization.
- Any impurities in the graft rubber should not inhibit anionic polymerization of caprolactam.
- Viscosity of the rubber dispersion in caprolactam should be low enough to be easily transported into the mold for polymerization.
- Shell composition of the core-shell graft should be conducive to promote adhesion at the nylon-rubber interface.

Attempts were made to address these issues during the course of this investigation.

The concept of toughening nylons with certain particulate rubbers has been successfully demonstrated by Baer.³ Graft rubbers with soft, crosslinked rubbery cores and hard thermoplastic shells of acid-functionalized copolymers have given blends of improved toughness and good properties when melt blended with nylon 6, 6 and its copolymers.

The above approach is not applicable to nylon 6 RIM system since the polymer is formed *in situ* in the mold. The chemistry of caprolactam polymerization is shown in Fig. 1. The only known successful means of toughening a nylon 6 RIM polymer is to copolymerize with low molecular weight polyethers or polybutadienes with terminal functional groups (Fig. 2).

Baer tried to extend the particulate graft rubber approach to toughen the nylon 6 RIM system,¹¹ with the premise that dispersion of rubber graft in caprolactam monomer ought to be easier than dispersing rubber graft in nylon matrix, since one no longer has to contend with polymer-polymer (i.e., grafted shell-nylon) miscibility but with a much favorable polymer-monomer miscibility (grafted shell-caprolactam). To this end, attempts were made to disperse the dried graft rubber crumb with the styrene-acrylonitrile shell in hot

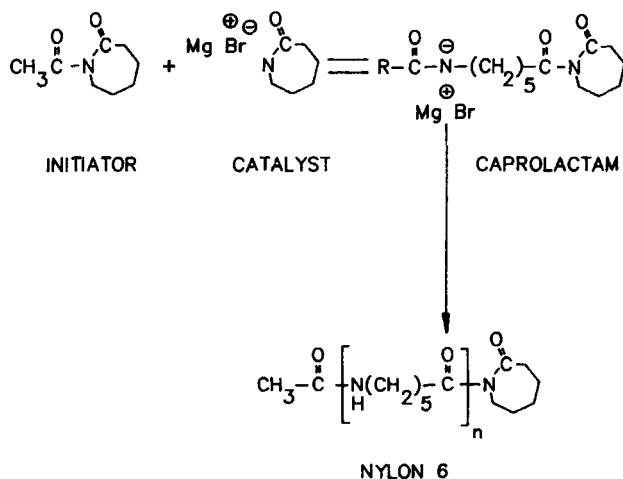
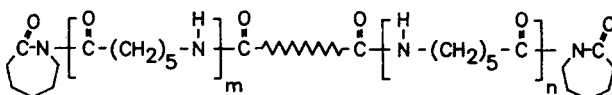
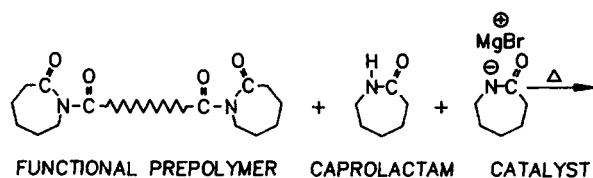


Fig. 1. Acyllactam-initiated anionic polymerization of caprolactam.



NYLON BLOCK COPOLYMER

Fig. 2. Synthesis of nylon block copolymer.

caprolactam monomer. Milky, translucent dispersions were obtained that appeared to be quite uniform and free from agglomerates to visual observation. Such dispersions, on polymerization, however, exhibited poor impact properties. Electron microscopy revealed (Fig. 3) that the rubber particles were present mostly as large aggregates in these samples, and the poor impact properties were explained as due to the nonuniform dispersion of rubber particles in nylon matrix. These castings, on injection molding, showed much

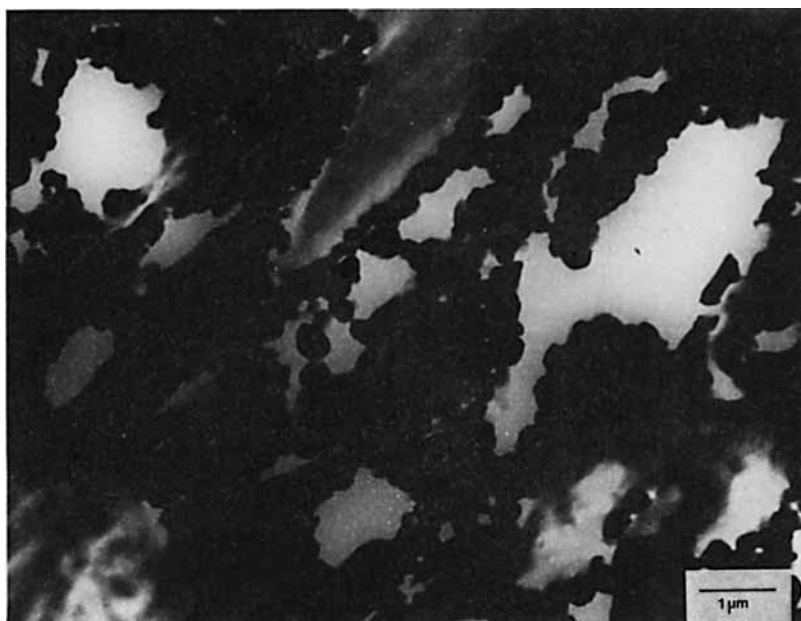


Fig. 3. Transmission electron micrograph of nylon 6 RIM modified with dried graft rubber crumb.

better impact strength, however. Enough shear was apparently being generated during the injection molding process to completely redisperse the rubber particles into their original colloidal size.

Dispersion of the dried graft rubber crumb in caprolactam monomer was believed to be colloidal, based on visual observation for lack of a valid experimental technique, particularly since caprolactam is a solid at room temperature. Although the poor impact properties obtained on the castings may have been partly a result of the reversal of the dispersion during the polymerization of caprolactam and the formation of nylon 6 spherulites, it is believed that a truly colloidal dispersion of rubber crumb in caprolactam, which is so very essential, may not have been attained. The dried graft rubber particles are likely to have undergone some sintering and aggregation during the coagulation, and subsequent vacuum drying steps and the shear generated during the dispersion in molten caprolactam (a low viscosity medium) may not have been sufficient to break the aggregates into colloidal particles.

In order to verify this hypothesis, graft rubber (E, Table I) similar in composition to the dried crumb referred to above, but in the form of latex, was dispersed in caprolactam, thus eliminating both the coagulation and drying steps. The dispersion so obtained containing 12% rubber, polymerized well to high caprolactam conversion (2-4% residual monomer). Such high monomer conversions are typical of anionic polymerization of caprolactam free of side reactions. Transmission electron micrograph of casting from graft latex dispersion is shown in Fig. 4. It is evident from the micrograph that the quality of rubber dispersion in this instance is much superior to that obtained by dispersing the dried rubber crumb (Fig. 3). The dispersion obtained from graft rubber latex on polymerization also exhibited higher impact strength (2.5 ft. lb/in.) than the dispersions from dried rubber crumb (< 1.0 ft. lb/in.).

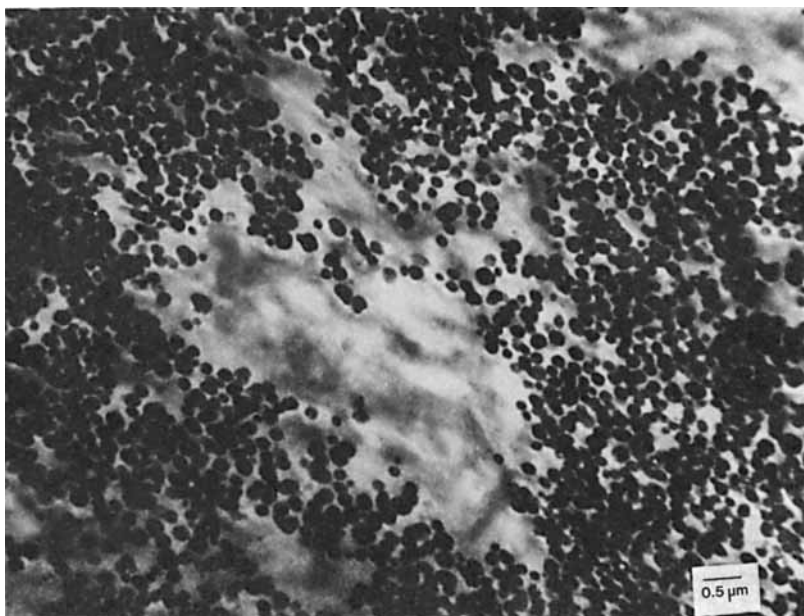


Fig. 4. Transmission electron micrograph of nylon 6 RIM modified with graft rubber latex.

TABLE IV
Properties of Particulate Rubber-Modified Nylon 6 RIM: Effect of Core/Shell Ratio^a

Core : shell	Tensile at fail (psi)	Elongation at fail (%)	Flexural modulus (psi)	Notched izod (ft lb/in.)
100 : 25	7500	27	340,000	2.4
100 : 40	7030	19.5	333,000	1.6
100 : 60	6370	21.0	305,000	1.1

^a % Rubbery core: 12.0; shell: S/AN = 70/30.

This compares favorably with the impact strength of a nylon 6 RIM modified with 10% polyether (2.0 ft. lb/in.).

The crystalline behavior of nylon 6 RIM containing 12% particulate rubber, determined by DSC, appears to be similar to that of a nylon block copolymer with 10% polyether prepolymer in terms of heats of fusion and crystallization, crystalline melting point, and crystallization temperature.

The rubber level employed in most of the modified nylons in this investigation is in the 10–15% range since it provided dispersions having sufficiently low viscosities. Dispersions of such graft rubbers at higher levels (e.g., 20% rubber) are too viscous and, when cast, trap air bubbles during polymerization resulting in castings with voids.

Effect of Core–Shell Ratio

The effect of core–shell ratio of the graft rubber on the properties of such graft-rubber-modified nylon is given in Table IV. Most of the initial screening work was carried out with a core–shell rubber with a Bd/AN (93/7) core and S/AN (70/30) grafted shell. The core/shell ratio was set at 100:25. This low level of shell in the graft rubber was deliberately chosen to maximize the effect of rubber with a minimal influence of the S/AN shell on the properties of nylon 6 RIM.

It is evident from the table that the overall property balance deteriorates slightly as the shell content in the graft rubber is increased. This is not surprising in view of the fact that S/AN and nylon 6 are not compatible, and, at constant rubber level, the amount of S/AN incorporated in the modified nylon increases with decreasing core/shell ratios. It is also possible that since the grafting efficiency decreases with increasing levels of grafting monomers, the ungrafted S/AN could act as stress concentrators to bring down the impact.

Effect of S/AN Ratio

The composition of the graft shell can be an important factor in determining the properties of the modified nylons. A certain degree of compatibility between the matrix nylon and the dispersed phase, and, in this case, the shell of the graft rubber, is essential to obtain a favorable interface. Polystyrene was chosen as the shell in one of the grafts in this series to stress this point, in view of its incompatible nature with nylon. But since polystyrene is soluble in hot caprolactam monomer, the dispersion turned out to be too viscous to

TABLE V
Properties of Particulate Rubber-Modified Nylon 6 RIM: Effect of Styrene/Acrylonitrile Ratio^a

S:AN	Tensile at fail (psi)	Elongation at fail (%)	Flexural modulus (psi)	Notched izod (ft lb/in.)
100 : 0	Too viscous			
90 : 10	7200	2.6	282,000	2.0
70 : 30	7500	27.0	340,000	2.4
40 : 60	Retarded polymerization			

^a% Rubbery core: 12.0; Core : shell: 100 : 25.

handle. Incorporation of 10% acrylonitrile in the shell brings about a dramatic change in the viscosity behavior of the dispersion. As the acrylonitrile level in the shell is increased, an overall improvement in properties is observed (Table V). However, when the acrylonitrile level in the shell is increased to 60%, the polymerization of the dispersion is retarded considerably. It is likely that the concentration of nitrile groups in this case is high enough to slow down the kinetics of polymerization. In view of the results, graft shell composition of 70S/30AN was employed in most of our work.

Effect of Reactive Monomer in Shell

Baer's earlier work³ on graft rubber dispersion in nylon polymers demonstrated that incorporation of an acid-functional monomer in the shell of the particulate rubber is required to achieve significant improvement in toughness. In the case of nylon RIM, since the polymerization of caprolactam takes place in the mold, any reactive (nonacidic) monomer in the shell of the graft rubber should ideally participate in the polymerization. Such a participation is believed to produce a desirable graft rubber-matrix interface.

Hydroxypropyl methacrylate (HPMA) was tried as a reactive monomer in the graft shell, and a noticeable increase in impact and elongation was observed (Table VI). Scanning electron micrographs of the fractured surfaces of particulate rubber-modified nylons in the presence and absence of HPMA in the shell are displayed in Figures 5 and 6. A diffused particulate structure with fuzzy boundaries is observed in the case where the graft shell has

TABLE VI
Properties of Particulate Rubber-Modified Nylon 6 RIM: Effect of Reactive Monomer in Shell^a

Shell Composition	Tensile strength (psi)	% Elongation (psi)	Flexural modulus (psi)	Notched izod (ft lb/in.)
(Nylon 6 RIM) (control)	9300	28	410,000	0.7
S/AN (70/30)	7500	27	340,000	2.4
S/AN/HPMA (60/30/10)	7950	51	305,000	5.4

^a% Rubbery core: 12.0; Core : shell: 100 : 25.

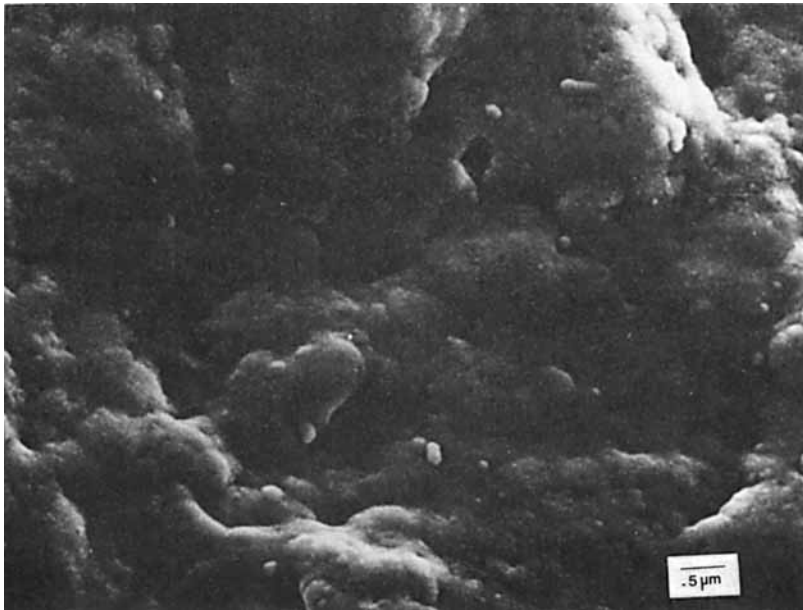


Fig. 5. Scanning electron micrograph of a fractured surface of a particulate rubber modified nylon 6 RIM with hydroxypropyl methacrylate in the graft shell.

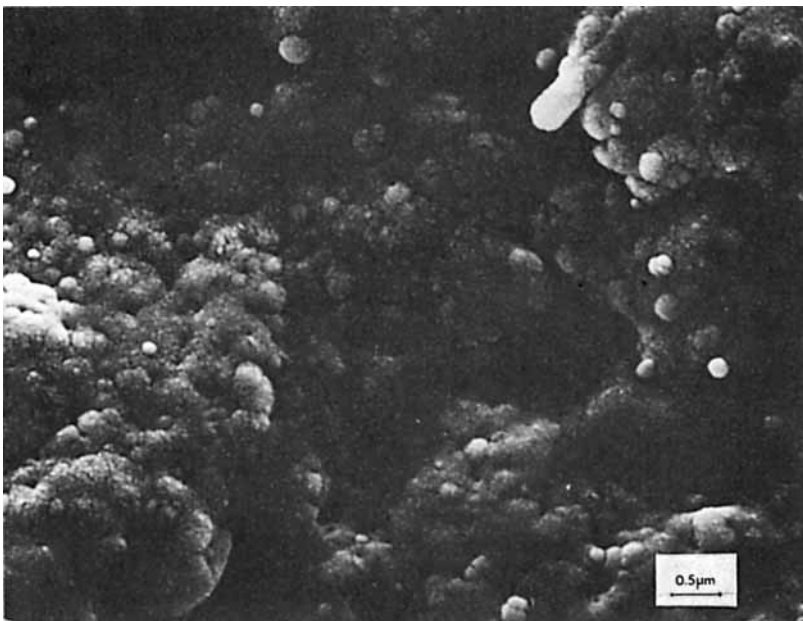


Fig. 6. Scanning electron micrograph of a fractured surface of a particulate rubber modified nylon 6 RIM without a reactive monomer in the graft shell.

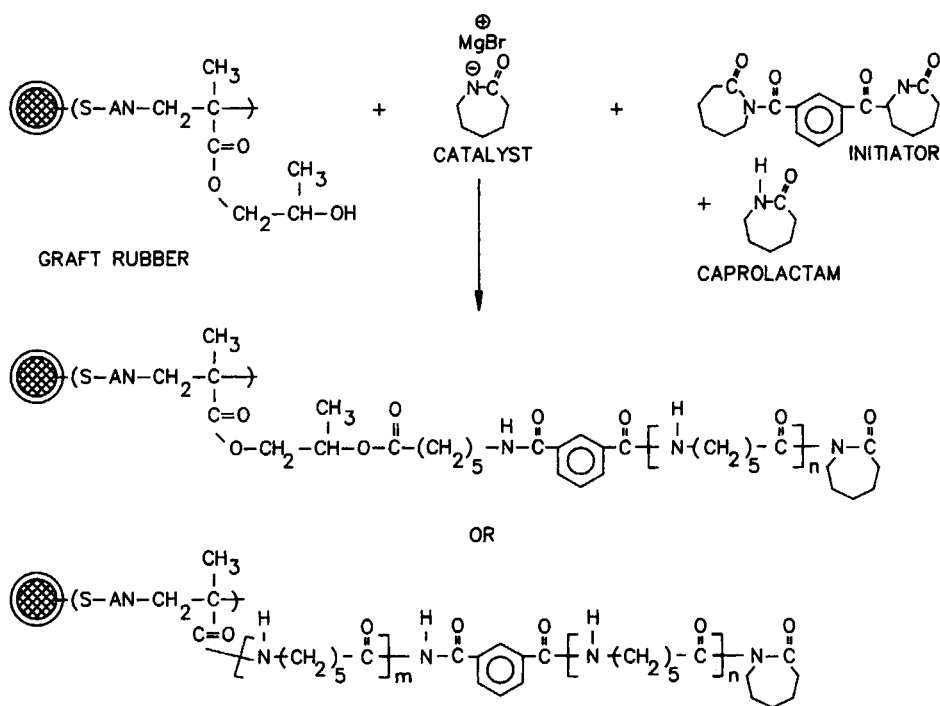


Fig. 7. Proposed mechanisms for reactive monomer participation in caprolactam polymerization.

HPMA; and, in contrast, graft rubber ($0.2 \mu m$) with distinct particulate identity can be seen in the case where the graft shell has no reactive monomer. No attempts were made to identify the actual interaction involved; but it is speculated that, in the case of hydroxypropyl methacrylate, there are two possible modes for this to occur: Viz. (i) the hydroxyl group can generate an alkoxide anion in the presence of Grignard to react with the acyl lactam group on the initiator molecule, and/or (ii) the growing polymer chain with an active amide anion can terminate by an attack on the methacrylate ester group (Fig. 7). In either case, a covalent bond is formed between the particulate rubber and the nylon.

CONCLUSIONS

—Core shell rubbers can be dispersed as a latex in caprolactam to provide high quality dispersion. The dispersions so obtained are stable during caprolactam polymerization, and the same is confirmed by transmission electron microscopy. The dispersed rubber does not seem to greatly alter the polymerization rate or the crystallization behavior of nylon 6 formed.

—Graft rubbers with butadiene/acrylonitrile (93/7) core and styrene/acrylonitrile (70/30) shell have provided castings having good balance of properties commensurate with rubber levels.

—Incorporation of small amounts of a reactive monomer, such as hydroxypropyl methacrylate in the shell, brings about a marked improvement in impact strength.

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