Graft Polymers with Macromonomers. I. Synthesis from Methacrylate-Terminated Polystyrene

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Synopsis

Pure graft polymers having uniform molecular weight polystyrene side chains were prepared by free radical copolymerization of methacrylate-terminated polystyrene macromonomers (MA-CROMER) with ethyl acrylate, butyl acrylate, or other suitable monomers. The MACROMER monomer was synthesized by living anionic polymerization under conditions that led to very narrow molecular weight distributions. Very effective end capping produced a material that was highly monofunctional. The graft copolymers were prepared by several techniques such as free radical solution polymerization, by aqueous suspension polymerization which produced beads, or by emulsion reactions which yielded stable latices. Polymerizations were reproducible. High conversion of the MACROMER monomer into pure graft polymers was achieved, and the product was contaminated with only a little homopolymer. The milled and molded phase-separated graft polymers had optical clarity and physical properties characteristic of polystyrene-reinforced triblock polymers. Compositions of 20–30% polystyrene were thermoplastic elastomers with good recovery. When polystyrene contents were increased, the graft products were strong, flexible thermoplastics with well-defined yield strengths and increased permanent set. Copolymers of polystyrene macromers with acrylonitrile or vinyl chloride produced transparent polystyrene homopolymer-free graft polymer products having improved processing over polyacrylonitrile or poly(vinyl chloride) homopolymers.

INTRODUCTION

Graft polymers rarely exhibit the excellent physical properties obtained from anionically synthesized block polymers because of the difficulty of preparing pure, well-defined products.[1-3] Generally, homopolymer is formed, backbone degradation may occur, or side chain grafts do not have controlled, monodisperse molecular weights. However, it will be shown that pure graft polymers with controlled graft structures can be prepared by polymerization of low molecular weight polymers having a polymerizable end group with monomers capable of free radical or ionic polymerization.

These macromonomers (trademark, MACROMER) of controlled, narrow molecular weights are prepared by anionic polymerization.[4,5] (MACROMER is a technology and trademark, developed at CPC International Inc., and is currently owned by Research Corporation, New York, NY.) Polystyrene, polyisoprene, or styrene/isoprene diblock macromonomers have been prepared and terminated with such polymerizable functional groups as α-olefin, vinyl alkyl ether, styryl, acrylate, methacrylate, maleic half ester, or epoxy.

The methacrylate-terminated polystyrene macromonomer of 13,000 molecular

weight shown below copolymerizes with various monomers by conventional free radical copolymerization:

$$sec\text{-Bu}\left[\text{CH}_2\text{---CH}\right]_{n \cong 125} \text{---CH}_2\text{CH}_2\text{OCC}\text{==}\text{CH}_2$$
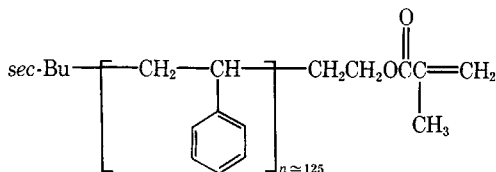
The MACROMER monomer is completely incorporated as a graft, even though the macromonomer double bond concentration is very low. Unlike most graft polymers, little or no graft homopolymer is present, and "grafts" are low molecular weight and monodisperse.

Microphase separation, morphology, and physical properties are largely controlled by the predetermined MACROMER monomer molecular weight. The monodisperse, low molecular weight polystyrene grafts aggregate into discrete domains of a few hundred Å dispersed in a continuous backbone elastomer comonomer matrix (Fig. 1). Each elastomer segment connected at both ends to a hard polystyrene domain is constrained from unrecovered viscous flow, and the polymer acts as a crosslinked elastomer.

Numerous graft polymer products are obtainable. Transparent, strong polystyrene-reinforced acrylic thermoplastic elastomers have been prepared, as well as poly(vinyl chloride) or polyacrylonitrile polymers containing pure polystyrene grafts. These thermoplastics possess the expected clarity of pure graft polymers and have greatly improved processing.

EXPERIMENTAL

Materials

Thiophene-free ACS grade benzene (Fisher Scientific) was purified by pumping through a column of Linde molecular sieves Type 4-A (Union Carbide)
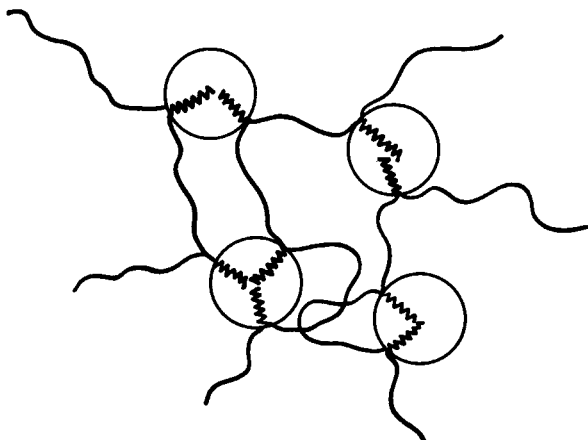

Fig. 1. Morphological structure of MACROMER monomer copolymers: (⌇) Macromer; (∼) comonomer; (○) domain.

and then through a column of calcium hydride particles (Fisher Scientific) to remove moisture and other materials having active hydrogens. The purified benzene had less than 10 ppm moisture.

Styrene monomer (Dow Chemical) was purified by pumping first through a calcium hydride column and then a column containing Amberlyst anion exchange resin A-27 (Rohm and Haas Co.). The purified styrene had less than 10 ppm moisture and 0–5 ppm inhibitor. The purified monomer was stored in oven-baked quart bottles under nitrogen.

Sec-butyllithium, purchased as a 12% solution in hexane from Foote Mineral Co., was used as received. The initiator was analyzed for active lithium by ASTM E233-64T.

Ethylene oxide (Eastman Kodak Co.), 1,1-diphenylethylene (Eastman Kodak Co.), and methacryloyl chloride (Epoxylite Corp.) were generally used as received.

Butyl acrylate and ethyl acrylate (Rohm and Haas Co. or Celanese) were low inhibitor grade monomers and were used as supplied.

Thiophene-free benzene and reagent grade methyl ethyl ketone solvents (Fisher Scientific Co.) used in free radical polymerizations were used as received.

The azobisisobutyronitrile initiator (VAZO 64) was obtained from E. I. DuPont de Nemours and Co. The lauroyl peroxide initiator (Alperox) was used as received from the Lucidol Division of Pennwalt Corp.

The suspension stabilizer was a partially hydrolyzed, medium-high molecular weight poly(vinyl alcohol), Lemol 42-88 (Borden Chemical Co.). Surfactants for the latex preparation were Igepal CO-880, a polyoxyethylated nonylphenol (GAF Corp.) and Ninate 401, a calcium dodecylbenzene sulfonate (Stepan Chemical Co.).

MACROMER Monomer Synthesis. Synthesis of Methacrylate-Terminated Polystyrene

MACROMER Molecular Weight 11,000 (S11MA)

The polymerization was carried out in a 100-psi 1-gal, stirred glass Chemco reactor with a steam-heated steel jacket. The reactor was additionally fitted with a dip tube, solvent inlet, syringe port, and cooling coils. The reactor was conditioned by stirring benzene, diphenylethylene, and excess *sec*-butyllithium overnight.

To the benzene-rinsed reactor was charged 2500 mL of purified benzene and 0.2 g 1,1-diphenylethylene. The impurities were titrated out by adding the *sec*-butyllithium slowly via syringe until a light tan-orange color is maintained. The retention of the color signifies that the impurities in the reactor have been reduced to an insignificant amount.

Next, 24 mL of 12% *sec*-butyllithium was charged to the reactor. This amount was calculated from the expression:

$$\text{degree of polymerization} = \text{mol monomer/mol initiator} \qquad (1)$$

Purified styrene (416 g) was then introduced to the reactor under nitrogen pressure at a controlled rate to maintain a reactor temperature of 40°C.
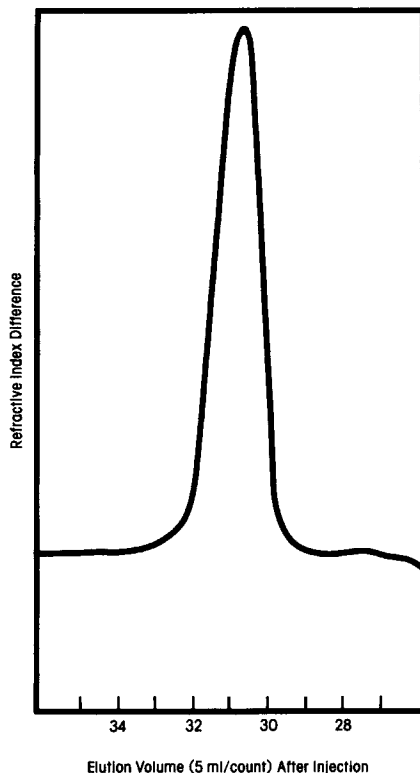
Fig. 2. GPC chromatogram of blend of nine S11MA Macromer runs

After 30 min, the reactor was cooled at 20°C and 5 mL liquid ethylene oxide was introduced via syringe. The disappearance of the orange color of the styryl anion signaled the formation of the alkoxy anion. The reactor was heated to 40°C, and the contents were then transferred under 20-psi nitrogen pressure into an oven-dried, nitrogen purged, serum-capped flask containing 10 mL methacryloyl chloride.

The MACROMER monomer was recovered by dropwise addition of the benzene solution to methanol. The precipitate was separated by vacuum filtration and dried at room temperature.

GPC chromatograms of nine independent runs of this S11MA macromonomer preparation showed very narrow molecular weight distributions. The average M_n was 11,200 and deviation was within the ±5% experimental error expected. A GPC curve of the blend of nine runs was as narrow as each sample (Fig. 2).

The MACROMER monomer is identified by the following code:

<div style="margin-left: 2em;">
S11MA: S = styrene
   11 = 11,000 g/mol molecular weight
   MA = methacrylate-terminated
</div>

MACROMER Monomer Polymerization

Copolymerization with Acrylic Monomers in Solution

A solution of 30 g S13MA polystyrene macromonomer in 95 g of methyl ethyl ketone was mixed with 1.0 g azobisisobutyronitrile in 5 g methyl ethyl ketone.

The solution was introduced to a quart bottle containing 70 g butyl acrylate, purged with nitrogen, capped with a Mylar-lined cap and rotated in a 65°C bottle polymerization bath for 16 h.

A viscous, gel-free polymer solution was obtained with 50.25% total solids (calcd: 51.24%). The solution had a very slight haze, but become clear when solids were reduced a few percent. Since the film was transparent, the MACROMER monomer conversion was concluded to be very high.

Copolymerization with Acrylic Monomers in Suspension

An aqueous stabilizer solution of 300 g distilled water, 3.0 g 5% Lemol 42-88 solution, and 1.6 g disodium phosphate was introduced into a rinsed and dried quart bottle, and the bottle capped with a cap containing a butyl rubber insert and Mylar inner lining. After purging the stabilizer solution with nitrogen for 45 min via syringe needles, a monomer solution of 25 g S11MA macromonomer, 37.5 g ethyl acrylate, 37.5 g butyl acrylate, 15 g benzene, and 0.112 g lauroyl peroxide was charged into the capped bottle with a syringe. The bottle was rotated at 30 rpm in a 55°C bottle polymerization bath for 17 h and then heated 3 h at 65°C and 5 h at 95–98°C.

The aqueous suspension was filtered through a 60-mesh screen, the beads washed with distilled water, and dried at room temperature. The yield of opalescent beads was 95.8 g, which corresponds to an acrylic monomer conversion of 96.5%. The milled and compression-molded product was a transparent elastomer with a tensile strength of 1410 psi and 790% ultimate elongation.

The same recipe was used to prepare a MACROMER monomer/copolymer in a 2-L stirred reactor. The reactor was an unbaffled glass resin kettle with paddle stirrer operated at greater than 230 rpm to avoid monomer pooling. Polymerizations were carried out under nitrogen for about 5.5 h at 60°C and finished at 90°C.

Preparation of Stable Copolymer Latex 12-1

A solution of 481.9 g boiled distilled water, 21.1 g 5% sodium bicarbonate, and 92.4 g 10% aqueous Igepal CO-880 was charged to a 3-L beaker and a nitrogen purge started. A solution of 184.8 g n-butyl acrylate, 184.8 g ethyl acrylate, 158.4 g S13MA polystyrene macromonomer, 52.8 g toluene, and 15.4 g Ninate 401 was added under agitation with an Eppenbach homogenizer and agitated 10 min. Then 27.1 g of a solution of 0.924 g lauroyl peroxide in 33.0 g toluene was added, and the entire contents stirred an additional 3 min while cooling.

The emulsion was charged into a 2-L glass resin kettle with a 3-in. turbine agitator and stirred rapidly under nitrogen while heating to 55°C. The agitation was reduced to 175 rpm while heating at 55°C for 3 h. The temperature was raised to 95°C and held for 30 min, and then the latex was cooled and filtered through cheese cloth. Monomer conversions and latex properties are reported in Table III.

Copolymerization with Acrylonitrile

Into a quart bottle was charged 30.0 g S11MA polystyrene macromonomer, 0.10 g azobisisobutyronitrile, 80 g acetone, and 40 g dimethylformamide. After

capping with a cap having a butyl rubber gasket and Mylar inner lining, the bottle was purged with nitrogen, and 30.5 g acrylonitrile was charged via syringe. The clear solution was polymerized 16 h in a 67°C bottle polymerization bath, and then heated an additional 6 h at 90°C.

The product, a swollen powder, was dried in a 50°C vacuum oven to give a yield of 55 g of pale yellow dried powder. When compression molded 5 min at 150°C and 30-ton ram pressure, the powder fluxed easily, and a brittle, transparent 10-mil film was obtained with a slight yellow color. The transparency of the film signified that little unreacted MACROMER remained.

Copolymerization with Vinyl Chloride

To an aqueous solution of 300 g distilled water, 3.0 g 5% Lemol 42-88, and 0.4 g disodium phosphate in a quart bottle was added 14.56 g S16MA macromonomer and 0.34 g lauroyl peroxide. The bottle was chilled in ice, vinyl chloride condensed in the bottle, and allowed to evaporate to the correct weight while driving out air. Then the bottle was capped with a butyl rubber gasketed, Mylar-lined cap, and rotated in a 55°C bath for 19 h. The excess vinyl chloride was bled off, and the beads filtered and rinsed with distilled water. The product yield was 92.5 g (91.2% vinyl chloride conversion). The GPC chromatogram showed no detectable unreacted MACROMER at 30.5 counts.

Analysis

Unreacted MACROMER monomer in the copolymers were determined on a Water Associates Gel Permeation Chromatograph using THF as the eluting solvent, 10^3, 10^4, 10^5, 10^6 Å porosity columns, and 1 mL/min flow rate. The MACROMER monomer peak area was calibrated from an average of several MACROMER monomer GPC standards by injecting measured volumes of MACROMER monomer solutions of known concentrations into the GPC. The unreacted MACROMER monomer in the copolymer samples were determined by injecting 2.00 mL of the copolymer solutions of known solids and calculating the areas of the free MACROMER peaks.

Physical Properties

The dried polystyrene macromonomer copolymers were milled for 2 min on a lab mill at 143–150°C unless otherwise specified. Sheeted products from the mill were compression molded 10 min at 170°C in 20-mil picture frame mold at 1100 psi.

Stress–strain data were obtained on an Instron Tensile Tester Model TTC at an extension rate of 10 in./min. Tensile specimens were cut from 20-mil compression-molded sheets using a dumbell die with a 1.6-in. constricted length. Permanent set, expressed as percent increase of the original length, was obtained from measurements of the increase in length of the elongated section of the specimen 24 h after tensile testing.

RESULTS AND DISCUSSION

MACROMER Monomer Functionality

Polystyrene macromers were synthesized by anionic initiation with *sec*-bu-tyllithium initiator which produced "living polymers" having reactive, unter-minated styryl anions.[4,6] The ratio of monomer to initiator controls the mo-lecular weight, and near monodisperse polymers are obtained if species reactive to anions are not present. End group functionality may then be introduced to the living polymer by terminating with active chlorine compounds or anhydrides such as methacryloyl chloride or maleic anhydride.

Simply reacting the living polystyrene with such compounds, however, gave rise to side reactions from styryl anion attack on the carbonyls or alpha hydrogens of the terminating agents. A strong bimodality in the GPC curves, NMR anal-ysis, and low functionality by copolymerization confirmed the existence of this problem. These side reactions were avoided by capping the strongly basic styryl anion with ethylene oxide before terminating. The living ethylene oxide anion, which is, of course, a weaker base, then reacted cleanly with the methacrylic halides. The resulting macromonomers were monomodal with very high mo-nofunctionality. Typically the M_w/M_n from GPC was about 1.05, and func-tionalities as estimated from copolymerization experiments were greater than 95%.

Demonstration of MACROMER monomer reactivity is evident from GPC chromatograms (Fig. 3). In this solution polymerization the methacrylate-terminated polystyrene macromonomer was 85.5% copolymerized at 75.6% butyl acrylate conversion. The MACROMER monomer is capable of being com-pletely copolymerized into the finished product (Fig. 4). On the other hand,
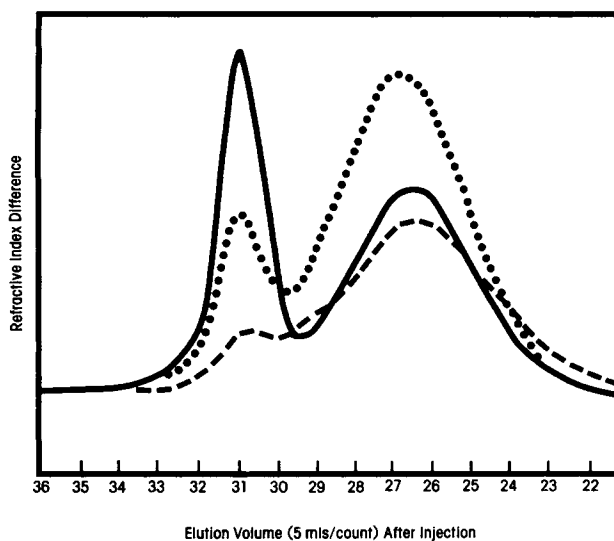

Fig. 3. GPC chromatograms of S11MA macromonomer/butyl acrylate (25/75) products at various conversions. Acrylic conversions: (———) 36.28%; (— — —) 62.3%; (- - -) 75.6%.
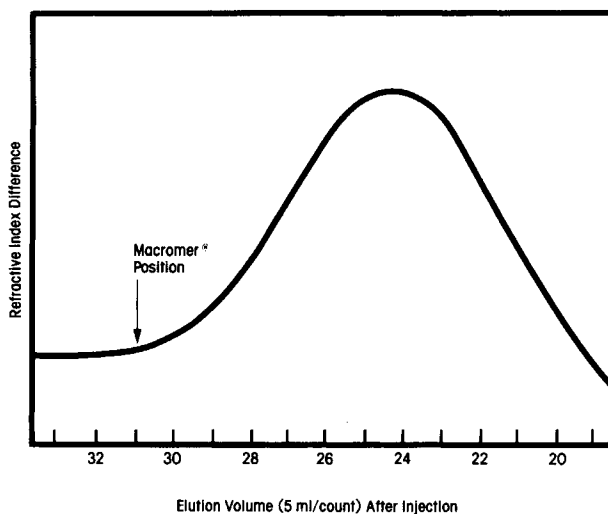
Fig. 4. GPC chromatograph of macromonomer latex copolymer 12-1.

a nonfunctional methyl-terminated polystyrene remained completely unreacted when copolymerized with acrylic monomer to high conversions.

Copolymerization Processes

Methacrylate-terminated polystyrene macromonomer readily copolymerized with various acrylic monomers by free radical processes to form acrylic polymers having uniform molecular weight polystyrene grafts. The polymerizations were carried out in conventional equipment, and special purification processes were not needed to prepare pure graft polymers.

These graft polymers were easily prepared in solution, but this process imposes limits on molecular weights because of solution viscosity. In order to achieve good physical properties in the macromonomer/acrylic copolymer, it is necessary for each acrylic elastomer backbone to contain at least two, and preferably more, polystyrene macromonomer "grafts." To assure this condition, especially at low MACROMER monomer levels in the copolymer, the molecular weight of the copolymer should be as high as possible. Solution polymerization is, therefore, considered less desirable.

Aqueous suspension polymerization most easily satisfied the requirements for obtaining high molecular weight polymers. An oil-soluble initiator, lauroyl peroxide, was used in order to avoid polymerization in the aqueous phase. Therefore, a new particle formation can be avoided, and the polymerization should take place entirely within the suspended monomer droplet to yield homogeneously sequenced copolymer beads.

Relatively large amounts of unreacted macromonomer in some of the products led to opaque or hazy milled and molded specimens. In these cases, incomplete MACROMER monomer conversion was attributed to macroscopic phase separation phenomena taking place during polymerization, which would be expected from known behavior of ternary polymer–polymer solvent systems.[7,8] Mixtures of two polymers in a common solvent generally have limited compatibility, and the solution separates into two liquid phases.[9] The polymers are unequally

TABLE I
Effect of Acrylate Comonomer Type and Composition and MACROMER Monomer Molecular
Weight on Product Uniformity

Polystyrene Macromonomer		Comonomer[a]	Appearance of milled and molded film
Molecular wt	Wt %		
11,000	45	BA	Transparent
11,000	45	EA	Opaque
16,000	45	BA	Transparent, very slight haze
16,000	45	1:1 EA:BA	Strong blue haze
16,000	30	1:1 EA:FA	Opaque
21,000	40	BA	Opaque

[a] n-Butyl acrylate (BA), ethyl acrylate (EA).

distributed in the two phases, and it has been shown that the separation process depends on the ratio of the polymers, their molecular weight, the nature of the solvent, and the total polymer concentration. Microphase separation of MACROMER monomer and acrylic segments in the newly formed polymer should also occur at some stage in the suspension droplet. At higher conversions the higher phase volume of the acrylic phase would favor partitioning more acrylic monomer into that phase and leave the macromonomer-rich phase relatively depleted of acrylic monomer. A significant amount of unreacted macromonomer would be expected to produce cloudy or opaque products due to the significant difference in refractive indices.

Accordingly, the molecular weight of the MACROMER monomer had a strong effect on product uniformity and appearance from the presence of unreacted macromonomer (Table I). GPC chromatograms showed the presence of more unreacted MACROMER monomer in copolymers with higher molecular weight macromers. Of course, the concentration of functional groups also decreases with increasing polystyrene size. Increasing polymer molecular weight in ternary systems is known to decrease compatibility in solution.[9,10] Higher molecular weight macromers undergo greater phase separation both during the polymerization and in the bulk product.

The copolymer product transparency is a function of the MACROMER monomer content incorporated. Higher macromonomer/acrylic feed ratios have lower ratios of polyacrylate/macromonomer phase volumes; therefore, macromonomer phases were probably depleted of acrylic monomer at higher monomer conversions.

The acrylic monomers also influenced MACROMER monomer conversion and product appearance. Whereas copolymerization with butyl acrylate produced the most transparent products, copolymers with ethyl acrylate were hazy or opaque. This difference is attributed in part to partial compatibility of polystyrene macromonomer in the butyl acrylate matrix. Ethyl acrylate copolymer had much greater opacity than the corresponding butyl acrylic copolymer, even though both contained the same amount of unreacted MACROMER monomer. The partial compatibility of polystyrene and polybutyl acrylate in bulk has been demonstrated by Kanig and Neff,[11] who found that solid blends of polystyrene and poly(butyl acrylate) resulted in reduction of T_g of the polystyrene phase.
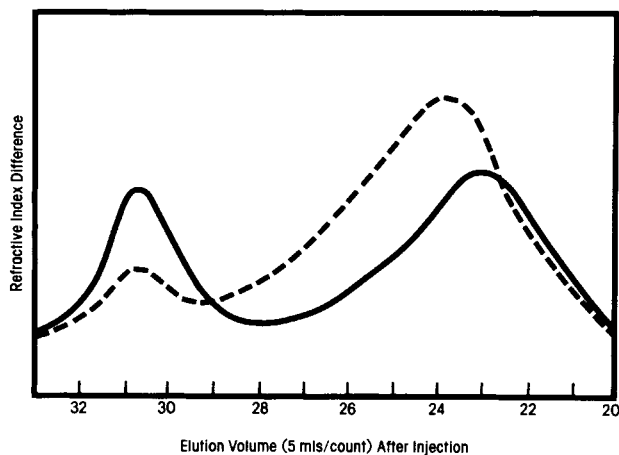
Fig. 5. GPC chromatogram of S11MA macromonomer ethyl acrylate (45/55) products prepared: (——) without benzene; (- - -) with benzene.

The presence of relatively low levels of benzene solvent in the suspension polymerization had a dramatic effect on reducing unreacted MACROMER monomer in the products (Fig. 5). Transparent products with high MA-CROMER monomer conversions were obtained in nearly all cases, and such elastomeric properties as permanent set were improved (Table II).

MACROMER monomer copolymers were prepared as stable, high solids lattices by a modified suspension polymerization process. Due to the inability of water-insoluble solids to diffuse through the aqueous phase, MACROMER monomer cannot be emulsion-copolymerized by conventional processes using water-soluble initiators. In order to prepare uniform-composition macro-monomer copolymer latex products, the emulsified monomer droplets must be formed with the total amount of MACROMER monomer uniformly distributed prior to polymerization initiation. Polymerization must be restricted to these sites, i.e., no particle nucleation must occur. Particle nucleation can be prevented by use of an initiator with low water solubility.

Polystyrene macromonomer was successfully copolymerized with acrylic monomers in latex form by emulsifying a monomer solution of the MACROMER monomer, and then heating the stable emulsion in the presence of a water-in-

TABLE II
Effect of Benzene Solvent on Copolymer Properties[a]

Polystyrene macromonomer			Appearance of milled and molded film	Tensile strength (psi)	Elong. (%)	Permanent set (%)
Molecular wt	%	Benzene % of acrylate				
16,000	35	0	Opaque	1600	450	90
16,000	35	20	Transparent	1880	410	43
16,000	30	0	Opaque	765	340	45
16,000	30	20	Transparent	1660	550	22
11,000	25	0	Hazy	1280	680	15
11,000	25	20	Transparent	1420	790	5

[a] Prepared with 1:1 EA:BA comonomers. Acrylic monomer conversions were all >95%.

TABLE III
Properties of Polystyrene Macromonomer Copolymer Latexes[a]

Polymer	6–14	6–19	12–1
Comonomer	BA	1:1 EA:BA	1:1 EA:BA
% Solids	39.2	43.6	43.6
Acrylate conversion (%)	98	96	95
MACROMER monomer conversion (%)	95	>94	ca. 100
pH	7.6	7.5	7.6
Coagulum (%)	0.0	0.0	0.0
Brookfield Visc., cps at 25°C (LVI spindle, 60 rpm)	11.9	20.4	20.7
Avg particle size (μm)	2	3–4	—

[a] Prepared with 30/70 S13MA macromonomer/acrylate.

soluble initiator such as lauroyl peroxide, under an inert atmosphere. The latexes were quite stable, and experienced only slight settling after 1–2 months (Table III). MACROMER monomer conversions were very high or essentially complete as shown by the complete disappearance of the S13MA macromonomer in the GPC trace at 30.5 counts (Fig. 4).

Acrylonitrile copolymerized readily with methacrylate-terminated polystyrene macromonomer in DMF solution, or as precipitation copolymerization in 2:1 acetone:DMF. These 10% and 50% macromonomer content products were easily molded into transparent but brittle films. The clarity of the films indicated that little or no unreacted polystyrene macromonomer was present.

Precipitation copolymerizations with acrylonitrile carried out in poor solvents such as benzene, acetone, or benzene/DMF resulted in compression-molded films exhibiting opaque areas from unreacted MACROMER monomer. The premature precipitation of the growing acrylonitrile polymer chain in poor solvents and the effect on MACROMER® monomer incorporation demonstrates the need for considering solvent effects on delaying phase separation in MACROMER monomer copolymerizations.

Physical Properties

The macromonomer copolymers prepared by suspension polymerization had high THF-insoluble gel contents. Whereas unprocessed polymer beads and unmilled molded specimens had gel contents ranging from 66% to 89%, milling on a 2-roll mill reduced gel contents to negligible levels in less than 2 min. The apparent high gel contents of the products indicate that considerable branching of acrylic polymer segments had occurred. After breakdown of the gel on the mill, the branched segments would probably have additional chain ends that do not contribute to effective network reinforcement.

The latex copolymers, unlike the suspension copolymers, were prepared essentially gel-free. Branching reactions were probably reduced by chain transfer to solvents or surfactants used in the process.[12]

Tensile properties and clarity of both suspension and latex copolymers generally were significantly improved when milled prior to compression molding the specimens (Table IV). Specimens molded without milling generally had surface irregularities or haze, and tensile properties were significantly poorer.

TABLE IV
Effect of Milling on Copolymer Physical Properties

| Polymer | Composition | Milled | Properties of molded specimens | | |
			Yield strength (psi)	Tensile strength (psi)	Elong. (%)
14–3	40 S11MA/60 BA	No	730	550	70
(suspension)		Yes	790	1420	540
14–12	50 S11MA/50 BA	No	1425	1170	190
(suspension)		Yes	1380	1890	400
12–1	30/S13MA/35 EA/35 BA	No	—	720	740
(Latex)		Yes	—	1450	940

Milling, extrusion, or molding thin specimens imposes shearing forces necessary to obtaining optimum properties. In addition to reducing gel in the suspension polymers, hot milling forces polystyrene flow, rearranges polystyrene domains, and establishes an interconnecting domain morphology in the product. The gain in physical properties from the network structure more than compensates for the expected loss in strength from increased chain ends.

The need to establish a monolithic network morphology for strength was demonstrated by comparison of a film cast from latex with that prepared from a toluene solution of a latex polymer. The latex-cast film was weak, but the solution-cast film was strong and elastomeric.

The polystyrene macromonomer copolymers possessed stress/strain properties expected of phase-separated, hard block-reinforced rubber-based block polymers
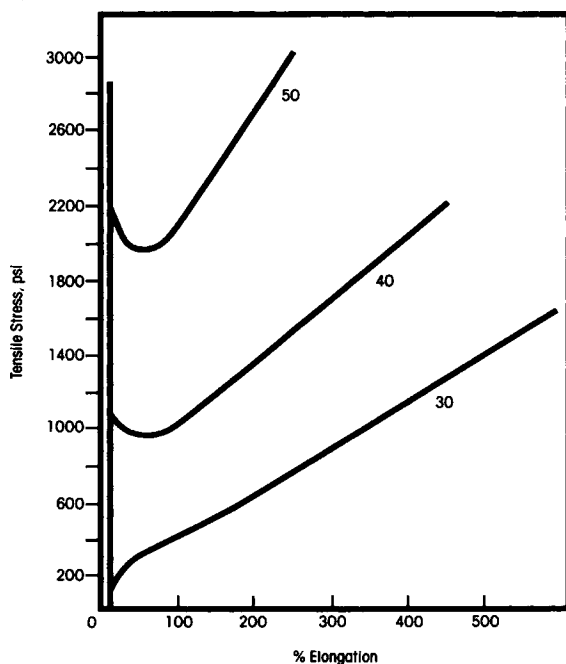

Fig. 6. Stress–strain Curves for 1:1 ethyl acrylate:butyl acrylate copolymers with S16MA Macromonomer at 30%, 40%, and 50% MACROMER monomer contents.

(Fig. 6). A definite yield was observed in specimens having greater than 30% MACROMER monomer, and yield strength increased with increasing MACROMER monomer content. Yielding is an expected phenomenon characteristic of triblock polymers, and has been shown to be due to a continuous phase of polystyrene blocks which is broken down on deformation.[13]

Thermoplastic elastomers with good recovery were obtained at lower MACROMER monomer levels (20–30%). The copolymers performed as flexible thermoplastics with higher tensile and yield strengths at 35–45% MACROMER monomer levels. They were ductile thermoplastics with high yield strengths and high permanent sets at 45–55% MACROMER monomer contents.

Acrylonitrile or vinyl chloride copolymers with methacrylate-terminated polystyrene macromers exhibited significant improvement in processing over the respective homopolymers. The 10% and 50% macromonomer-content acrylonitrile copolymers fluxed easily at 150°C and were easily molded into transparent, hard films. Polyacrylonitrile is well known to be difficult to mold without degradation.

The macromonomer/vinyl chloride copolymers did not require processing aids since the melt flow of the graft products were improved over the poly(vinyl chloride) homopolymer. Milled sheets and molded specimens of the graft copolymer had greater clarity than PVC homopolymer controls, even with low levels of copolymerized macromonomer.

CONCLUSIONS

Polystyrene macromonomers (MACROMER) with molecular weights of 10,000–21,000, narrow molecular weight distributions ($M_w/M_n < 1.05$), and essentially quantitative methacrylate monofunctionality (>95%) were synthesized by anionic polymerization with sec-butyllithium. Side reactions leading to low functionality and bimodality by attack of the styryl anion on the terminating agents were avoided by capping with ethylene oxide before terminating. Although only methacrylate-terminated polystyrene macromonomer was discussed, highly functional polystyrene or polydiene macromers have been successfully prepared with other polymerizable end groups, such as maleic half ester, and these will be discussed in future papers.

It has been established that these macromonomers reproducibly copolymerized with vinyl chloride, acrylonitrile, or acrylic ester monomers to prepare pure graft polymers contaminated with little or no MACROMER homopolymer. The free radical processes for synthesizing these graft polymers were conducted in solution, or as aqueous suspensions. Stable latices were obtained by employing water-insoluble initiators with certain aqueous surfactant systems. In order to effect high MACROMER monomer conversion in suspension or latex polymers, some benzene solvent is generally necessary to delay microphase separation which occurs during the polymerization.

Milling or other operations which impose mild shearing forces are desirable for processing these suspension or latex polymers. The flow of the polystyrene melt phase under shear appears to establish a desired morphology for network reinforcement by the polystyrene domains. When these conditions are met the graft polymers have clarity and physical properties characteristic of phase-separated block polymer systems.

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