

Emulsion Copolymerization of Vinylidene Chloride and Butyl Methacrylate, 83:17 in Mol %

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SYNOPSIS

Seven 35% solids, (83 : 17 in mol %), vinylidene chloride (VDC)–butyl methacrylate (BMA) copolymer latexes were prepared at 25°C using redox catalyst by batch and seeded semicontinuous emulsion copolymerization processes: one batch (G), one seeded batch (F), and five seeded semicontinuous polymerizations of five different monomer feed rates ranging from 0.27 (A) to 1.10 (E) wt %/min. All of the emulsion polymerizations gave stable latexes of almost 100% conversion with negligible coagulum and narrow particle size distributions. The kinetic studies of seeded semicontinuous polymerization A–E showed that the rates of polymerization (R_p) were controlled by the monomer addition rates (R_a), and polymerizations A–D (0.27–0.79 wt %/min) were under monomer-starved conditions; polymerization E (1.10 wt %/min) was in near-flooded condition. Significant differences were found in the physical and mechanical properties of the latex films, depending on the mode of monomer addition. Infrared spectroscopy, ¹³C solid-state NMR spectroscopy, X-ray diffraction, the T_g and T_m values by DSC, dynamic mechanical spectroscopy, and tensile strength measurement of the latex films post-heat-treated for 30 min at 70°C or aged for several months at room temperature demonstrated that batch polymerizations F and G gave copolymers of heterogeneous composition and a crystalline character. In contrast, semicontinuous polymerizations A–E gave copolymers of more uniform composition and an amorphous character.

INTRODUCTION

The principal advantages of emulsion polymerization as a process for preparing synthetic polymers are: (1) High molecular weight polymers can be produced with reasonable reaction rates; (2) the monomers can be added during the polymerization to maintain copolymer composition control. However, little has been published on the effect of nature of polymerization process on the polymerization kinetics of VDC-related polymerizations and the properties of the latex films.^{1–6} In VDC copolymerization,^{7,8} compositional drifts should be controlled, because copolymer fractions containing long VDC sequences have a tendency to crystallize easily, re-

sulting in poor solubility in solvent-based coatings, loss of film-forming ability in latexes, poor thermal stability, and poor color stability. The present work deals with the emulsion polymerization kinetics and the physical and mechanical properties of the 83 : 17 VDC–BMA latexes and latex films, prepared by different polymerization processes. The reactivity ratios determined in VDC (M_1)–BMA (M_2) emulsion copolymerization system were $r_1 = 0.22$ and $r_2 = 2.41$.⁹

EXPERIMENTAL

Materials

VDC (Dow Chemical Co.) was fractional distilled under nitrogen at 31.2°C after washing 20 wt %

aqueous NaOH solution. The freshly distilled fraction was immediately used for the experiments. *n*-BMA (Rohm and Haas Co.) was distilled under vacuum at 57 mm Hg and nitrogen. The fraction distilled at 66°C was stored in a refrigerator prior to use. Ammonium persulfate, sodium metabisulfite, and ferrous sulfate (Fisher scientific reagent grades) were used as the oxidant, reductant, and activator, respectively. Aerosol MA-80 (American Cynamid) was used as an emulsifier without further purification. Monomethyl ether of hydroquinone (Fisher scientific reagent grade) was used as a shortstopper for the gravimetric determination of conversion during the polymerization. Distilled-deionized water (DDI-water) and nitrogen gas of zero grade were used.

Emulsion Polymerization

The recipes used in making VDC-BMA latexes by both processes are given in Table I. The polymerization reactor was a standard 500-mL four-necked flask immersed in a constant-temperature bath at 25°C and equipped with a lunc-type Teflon blade, a glass stirrer fitted with a Teflon trubore adapter, a precise thermometer of 0.1°C scale, a spiral reflux condenser in which -15°C coolant circulating to prevent the VDC vapor during the polymerization, and a sampling device to withdraw the sample during the polymerization. For the batch polymerization, the total monomer mixture with DDI-water and emulsifier was added into the reactor at the beginning of the polymerization and polymerized by an addition of activator, oxidant, and reductant solution (dissolved in DDI-water) at 25°C. For the semicontinuous polymerization, the seed formation was first completed, and the remaining monomer mixture was

fed into the reactor at the constant feed rate using the compact syringe pump (Harvard Apparatus Co.) throughout the polymerization. For the seed formation, 10 wt % of the total monomer mixture (VDC = 4.0 g : BMA = 4.0 g), with DDI-water and emulsifier was charged and maintained under nitrogen atmosphere for 0.5 h, and polymerized by an addition of activator, oxidant, and reductant solution (dissolved in DDI-water) at 25°C. The formation of seed latex was entirely completed within 30 min. After the additional 20 min at 25°C, the remaining of the monomer mixture was fed into the reactor at the constant feed rate as shown in Table I, using the compact syringe pump throughout the polymerization. After the monomer addition procedure was finished, the polymerization was allowed to proceed for an additional 4 h to complete the reaction. The final conversion was measured gravimetrically.

Conversion Measurement

After the polymerization was started, 1–2 mL of the reaction mixture was sampled at appropriate intervals throughout the polymerization. The latex was placed in a tared aluminum weighing dish along with three drops of shortstop solution (0.06 g monomethyl ether of hydroquinone in 20 mL isopropanol) and dried in an oven at 70°C overnight. The percent solids and percent conversion of each sample were determined gravimetrically from the dried sample weights based on the total amount of monomer mixture in the recipe.

Physical Properties

Particle sizes of the latexes were determined by a Philips 300 transmission electron microscope

Table I VDC-BMA, 83 : 17 in Mol %, Polymerization Recipes by Batch and Semicontinuous Processes

	Semicontinuous ^b					Batch ^c	
	A	B	C	D	E	F	G
83 : 17 VDC-BMA ^a (wt %/min)	0.27	0.39	0.55	0.79	1.10	Seeded batch	Batch

^a Theoretical solids content: 35.0 wt %. Polymerization reaction temperature: 25.0°C.

^b Semicontinuous polymerization (A-E): monomer mixture 80.0 g; for seeding 8.0 g (VDC: 4.0 g, BMA: 4.0 g) [10% based on total monomer weight (80.0 g)]; for addition 72.0 g [90% based on total monomer weight (80.0 g)]. Emulsifier, catalyst, H₂O: the same as below.

^c Batch polymerization (G): monomer mixture 80.0 g (VDC: 61.6 g, BMA: 18.4 g); emulsifier, Aerosol MA-80, 1.6 g [(1.6% based on total monomer weight (80.0 g)]; catalyst: FeSO₄·7H₂O 2.20 × 10⁻³ g [(0.0027% based on total monomer weight (80.0 g)]; (NH₄)₂S₂O₈ 0.28 g [(0.35% based on total monomer weight (80.0 g)]; Na₂S₂O₅ 0.28 g [(0.35% based on total monomer weight (80.0 g)]; H₂O 152 g.

(TEM). A drop of latex with a concentration of 1–3% was placed on a carbon-coated Formvar electron microscope grid, and most of the drop was removed by contacting it with filter paper. The sample was then stained with 2% phosphotungstic acid (PTA) to improve the contrast. The transmission electron micrographs of the latexes were taken at room temperature. In order to calibrate the magnification of the electron microscope, a micrograph of a carbon replica of a diffraction grating was taken at the same setting as that used for the latex particles. The diameter of the latex particles was measured by a Carl Zeiss Mop-3 instrument. A computer program was used to determine the weight-average and number-average particle diameters, as well as particle size distributions. At least 500 particles were counted and their average values reported.

Fourier-transform infrared spectroscopy (Mattson Instruments Inc, Sirius 100) was employed to determine the crystallinity of the VDC–BMA copolymers prepared by both batch and semicontinuous polymerizations. VDC–BMA copolymer latex films before and after heat-treatment at 70°C for 30 min were used as specimens in the infrared spectroscopy.

¹³C-NMR spectroscopy was used to determine the sequence distributions of the 83 : 17 VDC–BMA copolymers, prepared by batch and semicontinuous polymerization. Liquid-state NMR spectrum of the 83 : 17 VDC–BMA latex copolymer prepared by semicontinuous polymerization was obtained using a Bruker WP 200 spectrometer operating at 50.32 MHz for carbon-13 at 50°C. A 20 wt % sample in deuterated nitrobenzene in a 10 mm diameter tube was used to reduce the total scan time and improve the signal to noise ratio. The sweep width of the spectrometer was 16,000 Hz, and a pulse with of 6 μ s (corresponding to a 45° pulse angle) was chosen; 16,384 data points were taken. A pulse delay of 10 s and gated decoupling were used to suppress the nuclear Overhauser enhancements (NOE) for quantitative measurements.

Solid-state NMR experiments were also performed using a General Electric NMR Instrument GN-300 spectrometer operating at 75.4 MHz for carbon-13 at room temperature. The standard cross-polarization magic angle sample spinning (CP/MASS) with spinning speeds of greater than 500 Hz were typical. The maximum ¹³C and ¹H RF field strengths were approximately 35 and 60 kHz, respectively. The CP contact time was 1 ms with a recycle delay of 6 s. For one-pulse experiments, the recycle delay was 30 s. Overnight accumulations of

approximately 10,000 (CP/MASS) and 2000 (one-pulse) transients were obtained. The sample volume was approximately 0.35 mL in a Doty Scientific, Inc., spinning assembly in a homemade probe. Deuterated benzene-swollen samples containing 50 wt % solvent were used. Acquisition times were approximately 40 ms (CP/MASS) and 80 ms (one-pulse).

The glass transition temperature (T_g) and crystalline melting temperature (T_m) of the VDC–BMA latex copolymers were determined using the Du Pont 1090 differential scanning calorimeter (DSC). Ten to 20 mg specimens were scanned as a heating rate of 20°C/min. The latexes were dried at room temperature to form films of about 1 mm thickness, which were heat-treated for 30 min at 70°C before use as the specimens.

X-ray powder diffraction patterns of PVDC⁷ and the VDC–BMA copolymers heat-treated at 70°C for 30 min were obtained with a Philips automated X-ray powder diffractometer using an Ni-filtered CuK α radiation; Sherrer–Debye ring patterns of these polymers were also taken.

Mechanical Properties

For mechanical studies, VDC–BMA copolymer latex films 3–4 mm thick were dried at 50°C in small polystyrene Petri dishes pretreated with a mold release agent for epoxy resin (Parafilm, Brice-Driscoll Corp.). These films were used for mechanical characterization after aging at room temperature for about a 4-month period to ensure that the further gradual coalescence and crystallinity were complete.

A Rheovibron viscoelastomer (Model DDV-II, Toyo Measuring Instrument Co.) was used to measure the storage modulus E' , the loss modulus E'' , and the loss tangent. The film was cut into 40 \times 6 \times 4 mm as specimens for dynamic mechanical spectroscopy. All measurements were made at 110 Hz, over a temperature range from –25 to 100°C, and at a heating rate of 1°C/min. T_g of all samples were determined from the peak on the loss modulus spectrum.

Tensile measurements were made at room temperature using an Instron tester (Instron Engineering Corp.). The films were cut to the size as described in ASTM D-1708 (for tensile measurements) using the microtensile specimen cutter. A crosshead speed of 0.5 in./min was found most suitable to cover the entire range of compositions of the copolymers. The Young's modulus E was determined from the initial slope of the stress–strain curve, and the energy to

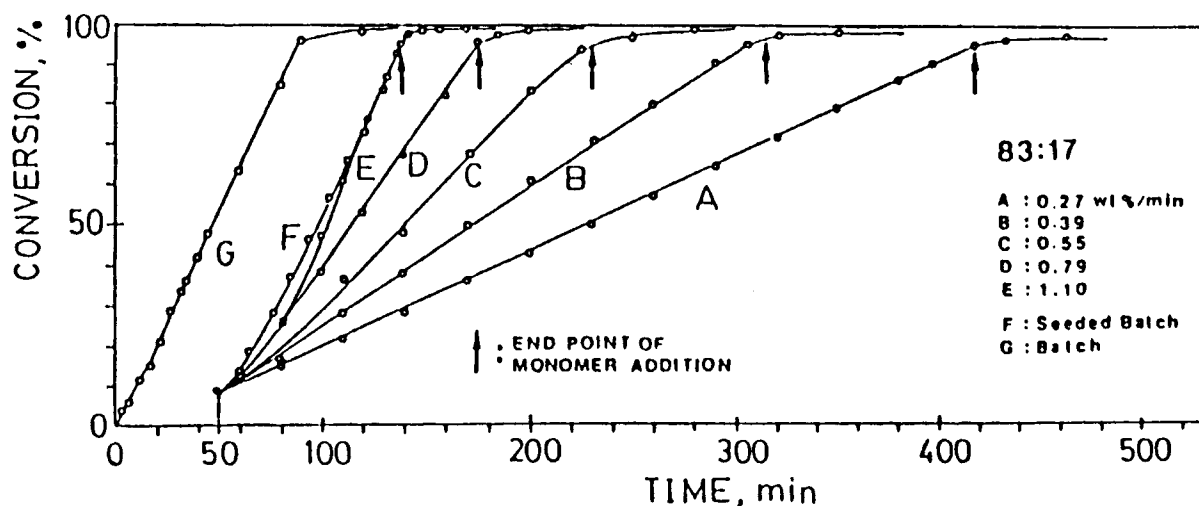


Figure 1 Overall conversion versus time curves of 83 : 17 VDC-BMA emulsion copolymerization.

break was determined from the area under the stress-strain curve. The ultimate strength and percent elongation were also determined. At least three specimens that did not have premature failure were obtained and their average values reported.

RESULTS AND DISCUSSIONS

Kinetic Study

All of the VDC-BMA emulsion polymerization carried out by both batch and semicontinuous polymerization at the present study gave stable latexes of almost 100% conversion with negligible coagulum. Figure 1 shows the overall conversion versus time curves of seven 83 : 17 mol % VDC-BMA emulsion copolymerization A-G as determined by the gravimetric method. In the seeded semicontinuous polymerizations A-E, the rate of polymerization (R_p) increased with increasing monomer feed rate (R_a), i.e., the rate of polymerization was controlled by the monomer feed rate. Specifically, the monomer feed rates in the polymerization A-D (1.40×10^{-4} mol $L^{-1} s^{-1}$) were less than the observed maximum rate of batch polymerization ($R_{p,max}$, 5.79×10^{-4} mol $L^{-1} s^{-1}$), indicating that the monomer concentration in latex particles in polymerizations A-D are much lower than those of the batch and seeded batch polymerizations G and F, respectively. In other words, the polymerizations A-D occurred under monomer-starved conditions.³ However, for the polymerization

E, which used the highest monomer feed rate (5.77×10^{-4} mol $L^{-1} s^{-1}$), the corresponding conversion versus time curve was nearly the same as those obtained in the batch polymerization G and the seeded batch polymerization F, indicating that the polymerization E occurred under near-flooded condition.⁴

Particle Size and Size Distribution

Table II shows the result of average particle diameters of 83 : 17 VDC-BMA copolymer latexes determined by transmission electron microscope (TEM). The copolymer latexes A-F prepared by seeded polymerization showed almost the same

Table II Particle Sizes of 83 : 17 VDC-BMA Polymer Latexes

Latexes	Particle Sizes		\bar{D}_w/\bar{D}_n
	\bar{D}_n (nm)	\bar{D}_w (nm)	
Seed	56	57	1.022
A	121	124	1.024
B	120	125	1.035
C	125	130	1.033
D	124	126	1.022
E	120	123	1.023
F	124	126	1.018
G	113	116	1.020

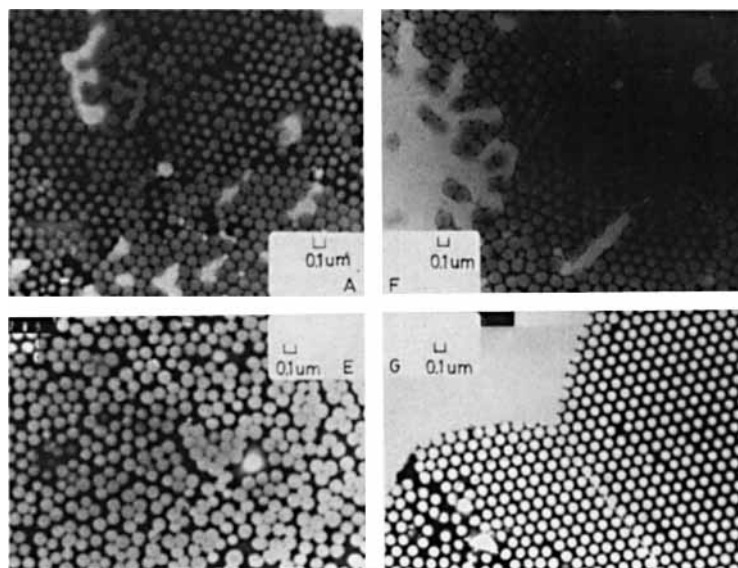


Figure 2 Transmission electron micrographs of 83 : 17 VDC-BMA copolymer latexes.

number-average particle diameters of about 120–125 nm, all with narrow size distributions. Figure 2 shows TEM pictures of these latexes. These results indicate that no secondary particle nucleation took place after the seeding process. The seeding with 10 wt % of the monomer ensured that most of the emulsifier was adsorbed on the particle surface, so that the secondary generation of new particles would be avoided. The polymerization G, carried out by conventional batch polymerization, resulted in a latex with a number-average particle diameter of 113 nm and a narrow size distribution. This average particle size was slightly smaller than those of the latexes prepared by seeded polymerization. VDC is much more water soluble than BMA (VDC = 0.25: BMA = less than 0.01, g/100 mL H₂O).^{8,10} If the copolymerization favors initiation in the aqueous phase (homogeneous nucleation),¹¹ the radicals generated in the aqueous phase add VDC monomer and polymerize until the oligomeric radicals exceed their solubility and precipitate. The precipitated oligomeric radicals adsorb emulsifier and absorb monomer to become primary particles. These primary particles formed in the early stage of polymerization may persist as nuclei for the capture of other primary particles. Therefore, in the copolymerization of VDC-BMA mixture, the number of nuclei generated would be proportional to the content of VDC monomer in the monomer mixture. In the same way, the latex G prepared by batch polymerization has a larger number of nuclei than those of latexes by seeded polymerization.

Physical Properties

Figure 3 shows a picture of the 83 : 17 VDC-BMA copolymer latex films A–G, heated for 30 min at 70°C, after dissolution in tetrahydrofuran (THF) at room temperature. A remarkable difference was found in solubility behavior of these latex films, according to the mode of monomer addition. The latex films F and G, prepared by seeded batch and batch polymerization, were found to be totally insoluble in THF at room temperature. In contrast, for the latex films A–E, prepared by semicontinuous polymerization, the solubility varied from totally soluble to partially insoluble with increasing monomer addition rate (R_d).

Figures 4 and 5 show the infrared spectra of the VDC-BMA copolymer latex films before and after heat treatment for 30 min at 70°C, respectively. The seven VDC-BMA copolymer latexes were all film-forming at room temperature. The infrared spectra of the latex films before the heat treatment did not show any of the characteristic crystallinity peaks that appear for poly(vinylidene chloride),^{12–14} independent of the method of the monomer addition. This seems to be an indirect indication that the latex particles do not contain crystalline domains as they are synthesized. However, the infrared spectra of the VDC-BMA copolymer latex films heat-treated for 30 min at 70°C showed that, although the VDC-BMA copolymers A–E, prepared by semicontinuous polymerization, still did not show any crystallinity peak, the VDC-BMA copolymers F and G prepared

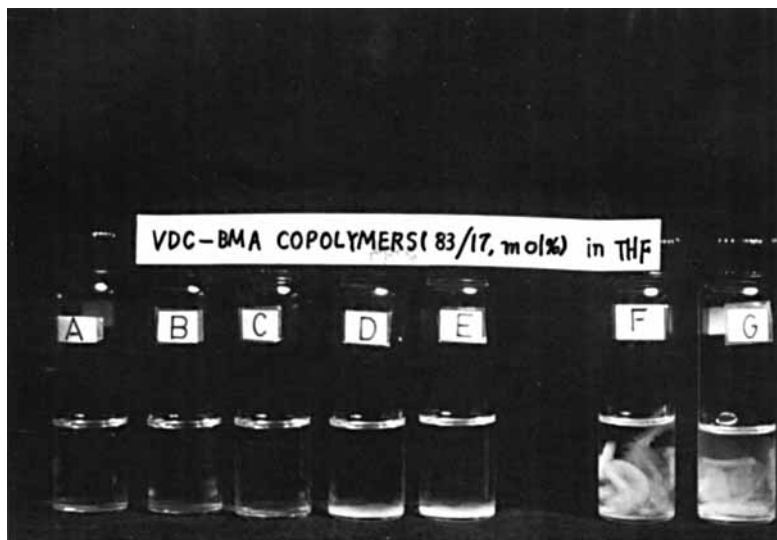


Figure 3 Solubility in THF of 83 : 17 VDC-BMA copolymer latex films (0.2 g latex films in 3 mL of THF).

by batch polymerization did show crystallinity peaks. These latex films were also aged for 6 months at room temperature as shown in Figure 6. Interestingly, these spectra were found to be similar to those obtained from the samples heat-treated for 30

min at 70°C as shown in Figure 5. It is known^{15,16} that the doublet at 1048 and 1070 cm^{-1} for the crystalline copolymers of vinylidene chloride is replaced by a single peak with the amorphous copolymers.

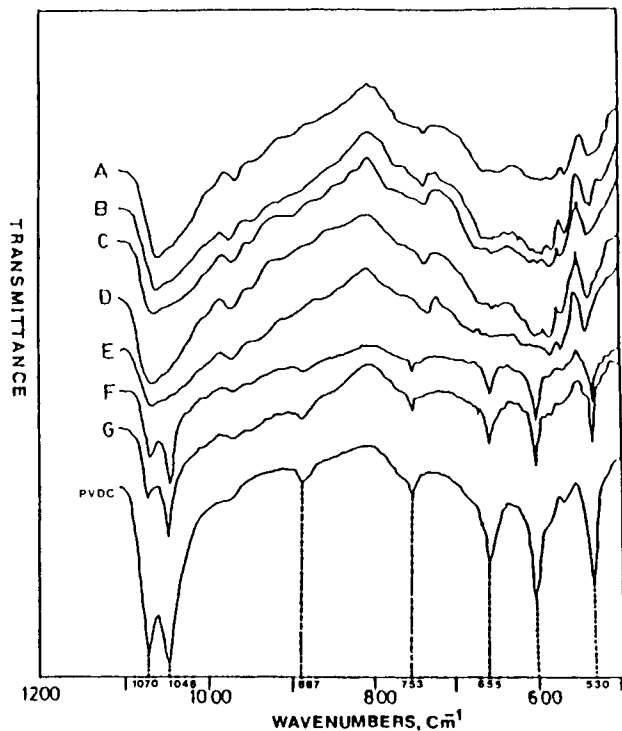


Figure 4 Infrared spectra of 83 : 17 VDC-BMA copolymer latex films A-G without heat treatment.

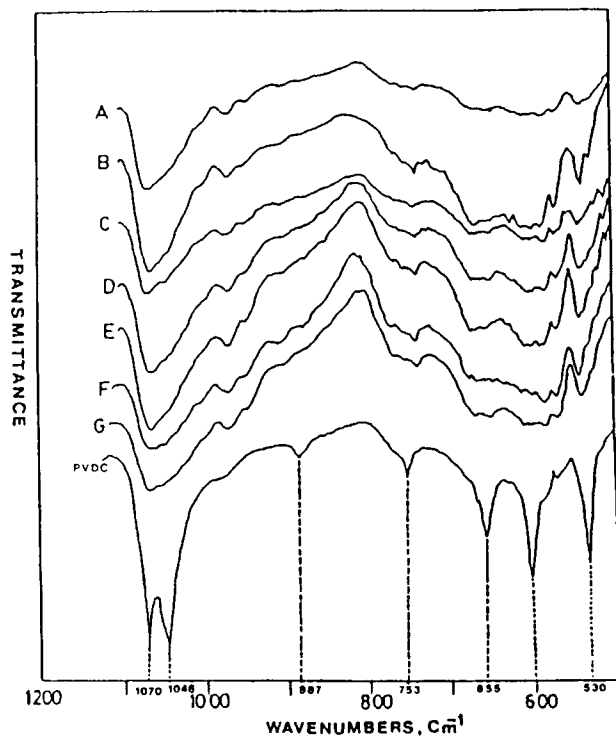


Figure 5 Infrared spectra of 83 : 17 VDC-BMA copolymer latex films A-G with heat treatment for 30 min at 70°C.

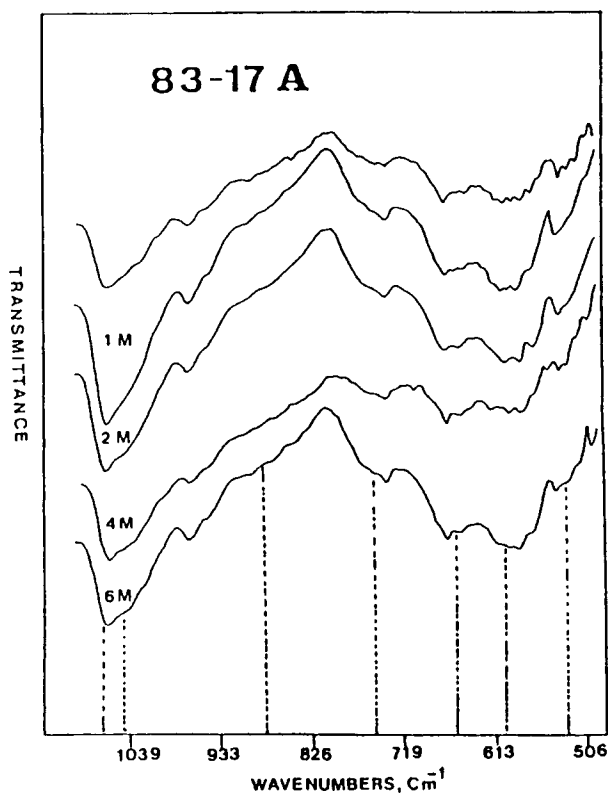


Figure 6 Infrared spectra of 83 : 17 VDC-BMA copolymer latex films A, F, and G, aged for 6 months (M) at room temperature.

The band at 1070 cm^{-1} is stronger than that at 1048 cm^{-1} for the unoriented crystalline samples, whereas the intensities are reversed as the unoriented are

oriented. In the infrared spectra of latex films F and G, heat-treated or aged for up to 6 months, the bands at 1070 cm^{-1} became weaker, while the band at 1048 cm^{-1} became stronger, indicating that these latex films were oriented under the heating and aging conditions, and became crystalline in character, i.e., crystallization took place. As only VDC can crystallize, these results indicate that, in the batch process, the copolymer composition drifted with conversion, resulting in copolymers having a fraction of chains containing long VDC sequences. On the other hand, in the semicontinuous process, the controlled monomer feed technique formed copolymers having shorter VDC sequences and with a more uniform copolymer composition, the length of the VDC sequences in the copolymer was controlled by the mode of monomer addition.

In the present study, ^{13}C liquid NMR spectroscopy was first used to determine the quantitative information of VDC-BMA copolymers, prepared by batch and semicontinuous emulsion polymerization. The 83 : 17 VDC-BMA copolymer prepared by batch polymerization, unfortunately, did not dissolve in any of the solvents at room temperature. At temperatures above 130°C , however, it did dissolve in nitrobenzene, with serious degradation and discoloration, and the evolution of hydrochloric acid. This insolubility gave much difficulties and unreliability for the quantitative analysis using ^{13}C liquid NMR spectroscopy. In contrast, the 83 : 17 VDC-BMA latex copolymer A, prepared by semicontinuous polymerization was clearly dissolved in nitrobenzene

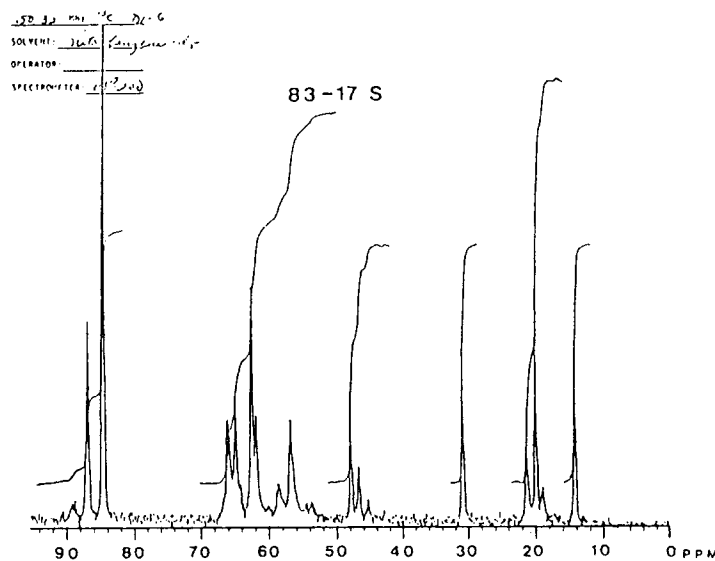


Figure 7 ^{13}C liquid NMR spectra of the 83 : 17 VDC-BMA copolymer A, prepared by semicontinuous polymerization.

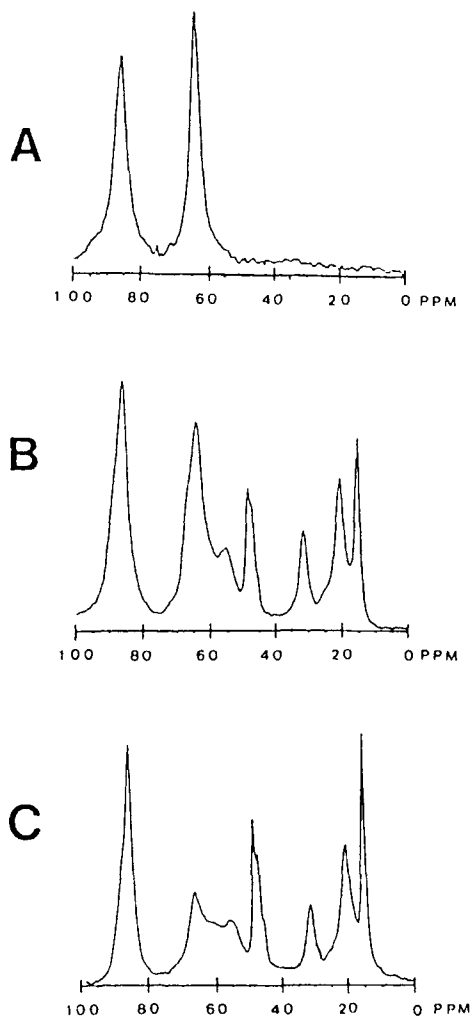


Figure 8 ^{13}C solid-state NMR spectra: (A) PVDC; 83 : 17 VDC-BMA copolymers G and A, respectively, prepared by (B) batch and (C) semicontinuous polymerization.

at room temperature. Figure 7 shows the ^{13}C liquid NMR spectrum of 20 wt % deuterated nitrobenzene dissolved 83 : 17 VDC-BMA copolymer A, prepared by semicontinuous polymerization.

Figure 8 shows the ^{13}C solid-state NMR spectra of PVDC and 83 : 17 VDC-BMA copolymers prepared by batch (G) and semicontinuous (A) polymerization, respectively, using the cross-polarization (CP) technique,¹⁷ which allows the detection of the immobile regions of the sample (i.e., the crystallites and their surroundings), in which the strong dipolar reaction remains. The resolution of these spectra was much poorer than that determined by ^{13}C liquid NMR for the 83 : 17 VDC-BMA copolymer A, prepared by semicontinuous polymerization as shown

in Figure 7. This poor resolution gave unreliable measurements of the quantitative analysis from solid-state NMR spectra.

Figure 9 shows the ^{13}C liquid NMR spectra of 50 wt % deuterated benzene-swollen or dissolved 83 : 17 VDC-BMA copolymers G and A, prepared by batch and semicontinuous polymerization, respectively. These spectra were obtained in a liquid one-pulse NMR experiment with magic angle spinning (high power proton-decoupling).¹⁷ It should be noted that the resolution of the spectra of these samples was much improved by using solvent-swollen samples, indicating that this technique yields much enhanced motion of the polymer molecules. It was also found that, for the 83 : 17 VDC-BMA copolymers,

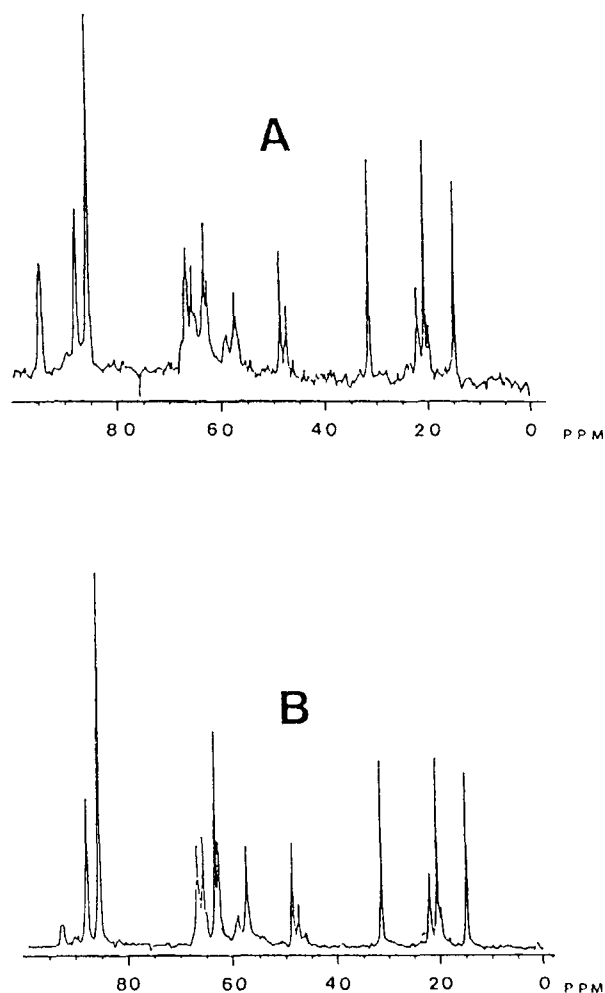


Figure 9 ^{13}C liquid NMR spectra of the 83 : 17 VDC-BMA copolymers G and A, prepared by (A) batch and (B) semicontinuous polymerization, obtained using solid-state NMR parameters.

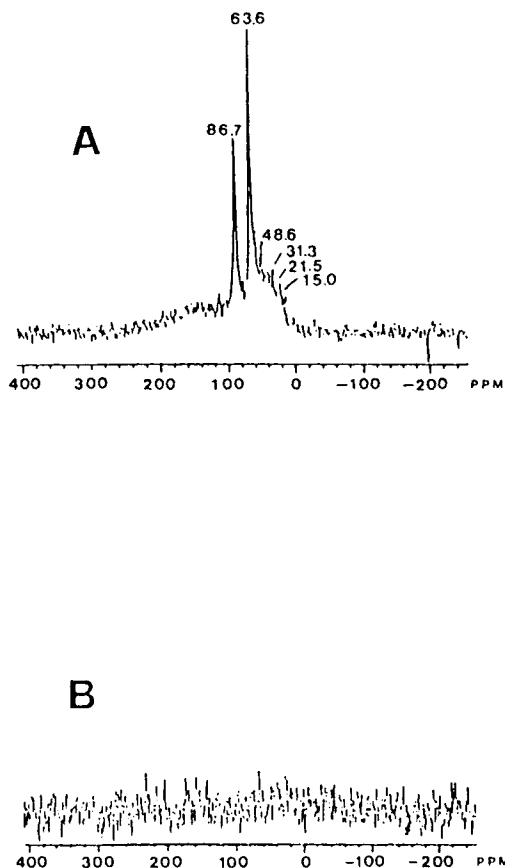


Figure 10 ^{13}C solid-state NMR spectra of deuterated benzene-swollen or dissolved 83 : 17 VDC-BMA copolymers G and A, prepared by (A) batch and (B) semicontinuous polymerization using the cross-polarization technique.

the semicontinuous sample gave a better signal to noise ratio than its batch counterpart, suggesting that the batch sample showed less molecular motion than the semicontinuous sample owing to the presence of crystallites in the batch sample.

Figure 10 shows the ^{13}C solid-state NMR spectra of 50 wt % deuterated benzene-swollen or dissolved 83 : 17 VDC-BMA copolymers G and A, prepared by batch and semicontinuous polymerization, respectively, using the cross-polarization (CP) technique. The batch sample showed two strong peaks at 63.6 and 86.7 ppm, which represent the chemical shifts of carbons of CH_2 and CCl_2 , respectively, in PVDC, and four small peaks at 15, 21.5, 31.3, and 48.6 ppm, which may arise from PBMA units adjacent to extended VDC sequences. These PBMA molecules have relatively small motions compared to BMA molecules in the amorphous regions. In contrast, the semicontinuous sample did not show

any significant peaks under the same CP technique. It is intrinsically difficult to obtain quantitative information from solid-state NMR technique.¹⁸ However, the differences between the spectra of the batch and semicontinuous samples suggest that the batch sample have much less molecular motion due to the presence of the crystallites.

Figure 11 shows X-ray diffraction pattern and Scherrer-Debye ring pattern of the VDC-BMA copolymer latex films heat-treated for 30 min at 70°C. Latex films F and G, prepared by batch polymerization, showed the same diffraction peaks and regular ring patterns as the PVDC, indicating that these copolymers are crystalline in character. In contrast, latex films A-E, prepared by seeded semicontinuous polymerization, did not show any characteristic crystalline peaks or regular ring patterns, indicating that these polymers are amorphous in character. These results are consistent with those of the infrared spectroscopy.

Table III shows the glass transition temperature (T_g) and the crystalline melting temperature (T_m) determined by DSC (heating rate, 20°C/min) for the seven latex films heat-treated for 30 min at 70°C. Latex films A-E, prepared by seeded semicontinuous polymerization, showed almost the same 16–17°C T_g value. In contrast, latex films F and G, prepared by batch polymerization, showed T_g values 7–8°C higher than those for the copolymers prepared by semicontinuous polymerization. Only the latex films F and G, prepared by batch polymerization, showed crystalline melting temperatures of 184 and 187°C, respectively. The difference in melting temperatures between the latex films F and G, prepared, respectively, by the seeded batch and batch polymerization, might be due to the difference in size of the crystallites present in copolymers. The difference in T_g between the latex films prepared by the two polymerization processes and the presence of T_m in batch latex films reflect that in the batch polymerization the copolymer composition drifted with increasing conversion, resulting in copolymers having a fraction of chains containing VDC sequences long enough to crystallize. In the semicontinuous polymerization, on the other hand, the corresponding copolymer compositions were more homogeneous, the VDC sequences were shorter, and the resulting copolymers were amorphous in character. The reason that the latex films prepared by batch polymerization have T_g values 7–8°C higher than the latex films prepared by semicontinuous polymerization might be explained by the presence of crystallites in batch copolymers which reduce the mobility of amorphous

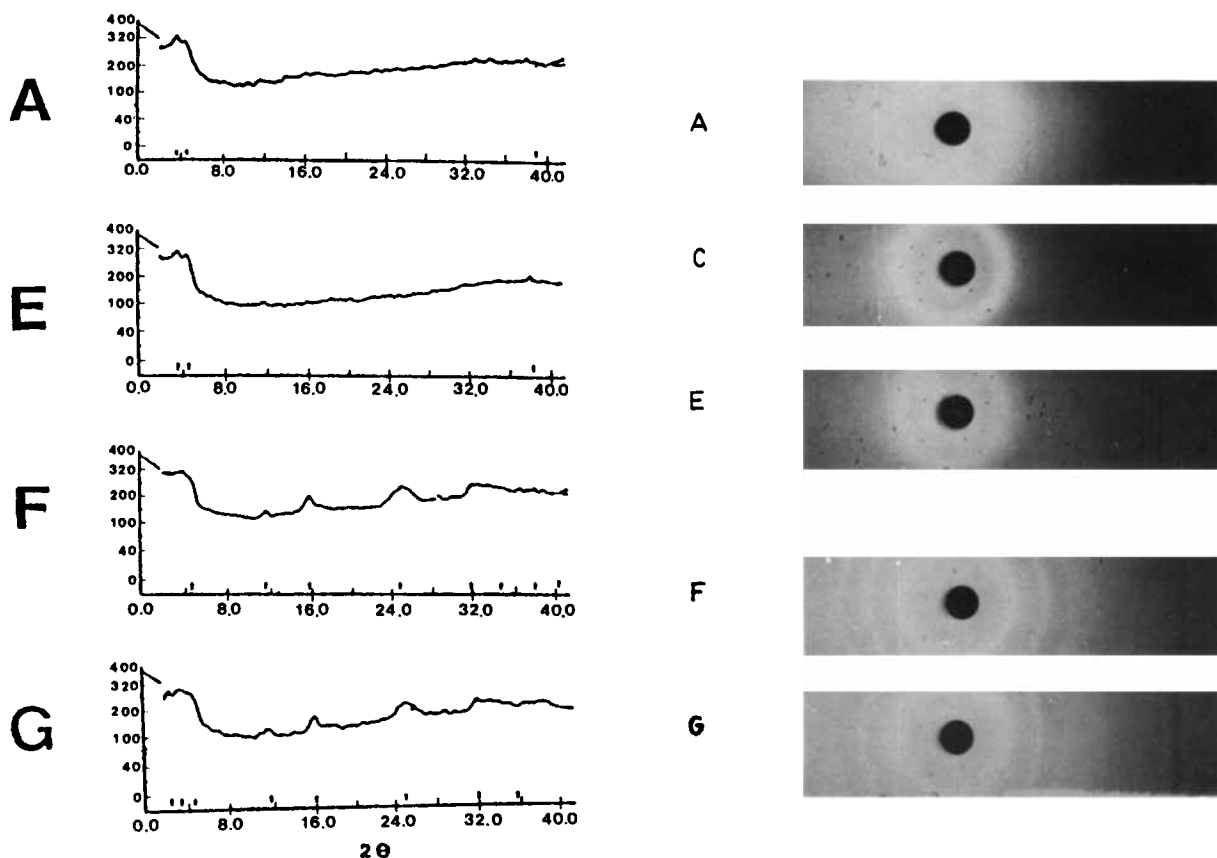


Figure 11 X-ray diffraction patterns and Scherrer-Debye ring patterns of 83 : 17 VDC-BMA copolymer latex films heat-treated for 30 min at 70°C.

chains trapped between crystallites, thereby increasing the T_g .¹⁹

It should also be noted that, for the latexes F and G, prepared by batch polymerization, which are film-forming at room temperature with amorphous character, the corresponding latex films heat-treated or aged at room temperature, however, were crystalline in character, having many valuable properties such

as low permeability against most gases and vapors, solvent resistance, and good mechanical properties.

Mechanical Properties

Figure 12 shows the results of the dynamic mechanical analysis using the Rheovibron viscoelastomer at 110 Hz and a heating rate of 1°C/min. The latex films A-E, prepared by seeded semicontinuous polymerization, showed almost the same 30–31°C T_g value. In contrast, the latex films F and G, prepared by batch polymerization, showed a T_g about 10°C higher than those of the latexes prepared by semicontinuous polymerization. The results are similar to those of the T_g values determined by DSC. The latex films prepared by both batch and semicontinuous polymerization showed one peak in loss modulus spectra. That might be due to the small difference in T_g between the homopolymers of VDC and BMA. The width of the peaks in the loss modulus spectra of the latex films A-E, prepared by semi-

Table III T_g and T_m Values for Heat-Treated 83 : 17 VDC-BMA Copolymer Latex Films^a

	Semicontinuous					Batch	
	A	B	C	D	E	F	G
T_g (°C)	16.3	16.3	15.8	15.7	16.9	23.2	24.2
T_m (°C)	=	=	=	=	=	=	=
MFFT	+	+	+	+	+	+	+

^a =: no T_m observed; +: lower than 5°C.

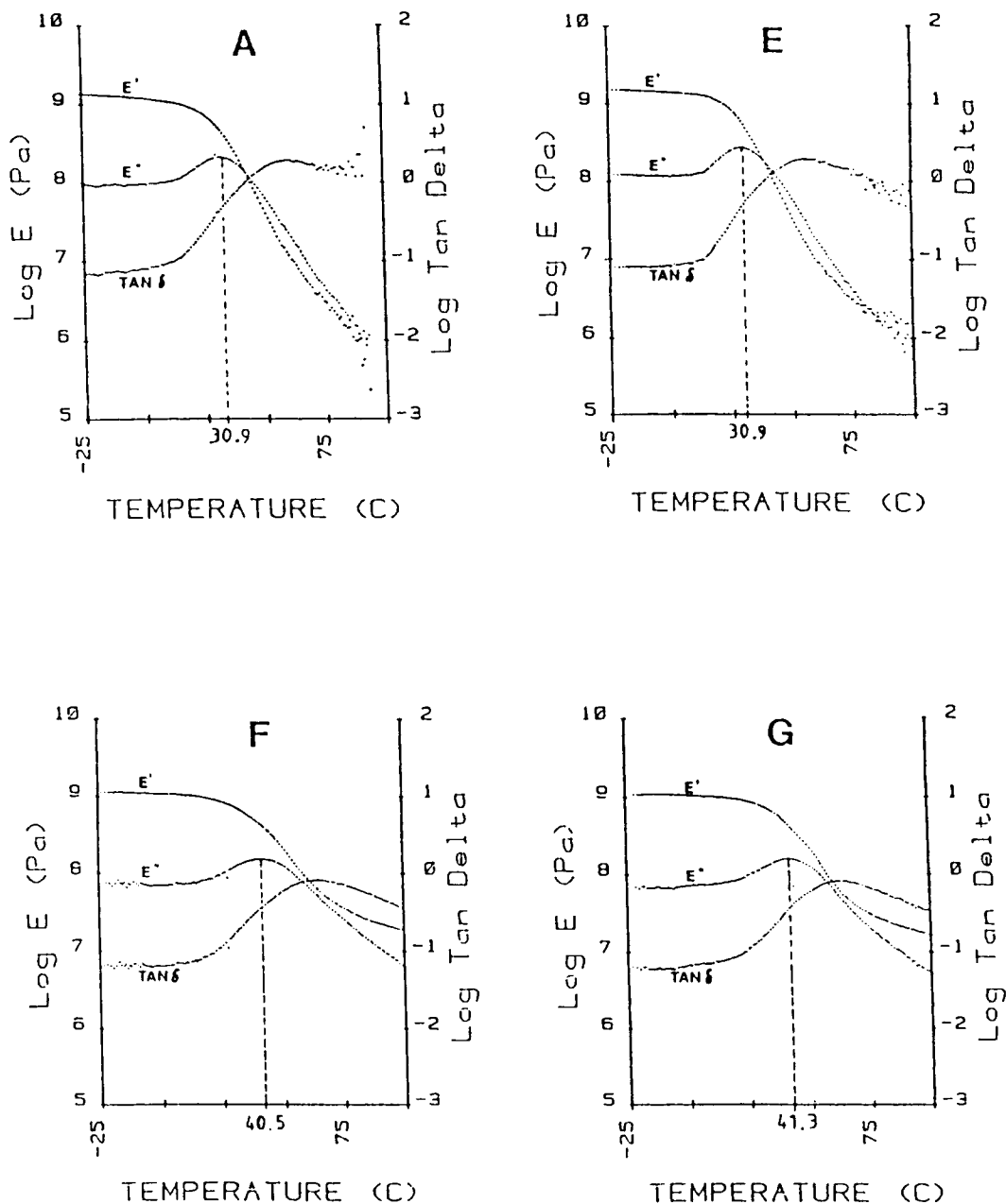


Figure 12 Dynamic mechanical spectra of 83 : 17 VDC-BMA copolymers A, E, F, and G.

continuous polymerization, however, were narrower than those of the latex films F and G, prepared by batch polymerization, indicating again that the copolymers prepared by semicontinuous polymerization have more homogeneous copolymer compositions than their counterparts by the batch polymerization. The storage modulus E' in the latex films A-E, prepared by seeded semicontinuous polymerization, approached a value of about 10^6 Pa at 100°C

with scattered data points, whereas the storage modulus E' in the latex films F and G, prepared by seeded batch and batch polymerization, respectively, approached a value of $10^{7.3}$ at 100°C with nonscattered data points, indicating that the latex copolymers F and G have higher moduli at temperatures above T_g . The latex copolymers F and G were found to be crystalline, as confirmed by the presence of T_m , higher T_g values, and the presence of crystalline

Table IV Tensile Properties of 83 : 17 VDC-BMA Copolymer Latex Films

Process	Semicontinuous					Batch	
	A	B	C	D	E	F	G
Young's modulus, $E^{a,b}$ (MPa)	3.4	6.2	7.3	12.7	12.7	230.1	296.3
Ultimate strength, σ_u^b (MPa)	1.3	2.7	2.7	2.9	2.9	7.6	8.4
Elongation to break, χ_u (%)	588	483	480	480	468	74	87
Energy to break, τ^b (MJ/m ³)	15.6	11.4	9.9	8.3	7.7	5.4	6.1

^a Determined from the initial slope of the stress-strain curve.

^b Based on the initial cross-sectional area.

characteristic peaks in the infrared spectra and X-ray diffraction patterns. The crystallites in crystalline material may act as a reinforcing filler or crosslinker¹⁹ between the amorphous regions, and increase the modulus and the stiffness in the composites. That might be the reason why the copolymers F and G have higher moduli, and more hardness at temperatures above T_g than their counterparts prepared by semicontinuous polymerization.

A significant difference was also found in tensile properties of these latex films. Table IV shows the results of the tensile measurements for 83 : 17 VDC-BMA copolymer latex films A-G, all dried at 50°C and aged for about a 4-month period. The latex films, prepared by semicontinuous polymerization, were flexible and tough, which might be explained by the homogeneous monomer compositions in copolymers, whereas the latex films, prepared by batch polymerization, were hard and stiff, which might be explained by the presence of the crystallites acting as reinforcing fillers or crosslinkers in the copolymers. The tensile properties of latex films A-E, prepared by semicontinuous polymerization, varied also with the monomer addition rate in the polymerizations. The Young's modulus and ultimate strength increased, and the percent elongation and toughness decreased with increasing monomer addition rate. The results indicate that the unit length of VDC molecule in copolymers is controlled by the monomer feed rate.

CONCLUSIONS

The method of monomer addition is found to have a remarkable effect on the kinetics of VDC-BMA

emulsion copolymerization, as well as the physical and mechanical properties of VDC-BMA latex copolymer films. The VDC-BMA copolymer latex films, prepared by monomer-starved semicontinuous polymerization, in general, were much more homogeneous in composition and amorphous in character. In contrast, the VDC-BMA copolymer latex films, prepared by monomer-flooded batch polymerization were much more heterogeneous and crystalline in character.

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