

Batch and Semicontinuous Emulsion Copolymerization of Vinylidene Chloride and Butyl Methacrylate. II. Physical and Mechanical Properties of Copolymer Latex Films

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SYNOPSIS

Vinylidene chloride (VDC)–butyl methacrylate (BMA) copolymer latex films of various compositions (83 : 17, 60 : 40, 33 : 67 in mol %), prepared by batch and semicontinuous processes, were investigated for their physical properties by infrared spectroscopy, ¹³C solid-state NMR spectroscopy, X-ray diffraction, solubility in various solvents, differential scanning calorimetry (DSC), and water vapor transmission rates (WVTR), and for their mechanical properties by dynamic mechanical spectroscopy (DMS), and tensile strength measurements. Semicontinuous latex films were found to be homogeneous in composition and amorphous in character. On the other hand, batch latex films containing high VDC monomer content were heterogeneous in composition and crystalline in character. These differences were found to reflect the effect of mode of monomer addition during the emulsion polymerization process, and correlated well to the results on kinetics, colloidal, and surface properties of the VDC–BMA copolymer latexes, as described in the first part of this study.

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 and (2) the monomers can be added during the polymerization to maintain copolymer composition control. It is well known that the mode of monomer addition has a great influence on the morphology and mechanical properties of such polymer films.^{1–7} However, little has been published on the effect of the nature of polymerization process (batch, semicontinuous, or continuous processes) on the properties of vinylidene chloride (VDC) copolymer films. In VDC copolymerization composition drifts should be controlled,^{8–14} because copolymer fractions containing long VDC sequences have a tendency to crystallize

easily, resulting 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 physical and mechanical properties of the VDC–butyl methacrylate (BMA) latex films with various copolymer compositions, prepared by batch and semicontinuous processes.

EXPERIMENTAL

Latex Preparation

A series of latexes having different compositions of VDC and BMA was prepared as shown in Table I. Emulsion polymerization was carried out in two different ways: the conventional batch process, where all the ingredients are charged initially into the reactor; and the seeded semicontinuous process, where the monomer mixture is added at a constant feed rate after the formation of seed latex. The experimental details have been described in a previous paper.¹⁵

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Table I Polymerization Recipes of VDC-BMA by Batch and Semicontinuous Processes^a

	Mol %			Ingredients
	VDC	BMA		
1	100	0	B	Batch
2	83	17	B (G) SB (F) S ^a (A-E)	Monomer mixture: 80.0 g Emulsifier: Aerosol-MA (80%), 1.6 g (1.6%) ^b Catalyst:
3	60	40	B	FeSO ₄ · 7H ₂ O, 2.20 × 10 ⁻³ g (0.0027%) ^b (NH ₄) ₂ S ₄ O ₈ , 0.28 g (0.35%) ^b Na ₂ S ₂ O ₅ , 0.28 g (0.35%) ^b H ₂ O: 152.0 g
4	33	67	B S	Seeded Monomer mixture: 80.0 g Monomer for seeding: 8.0 g (VDC = 4.0 g, BMA = 4.0 g) (10%) ^b Monomer for addition: 72.0 g (90%) ^b
5	0	100	B	Emulsifier, catalyst, H ₂ O: the same as above.

^a B = Batch polymerization, S = seeded semicontinuous polymerization: 0.27 wt %/min in monomer feed rate, SB = seeded batch polymerization; S^a = for 83 : 17 VDC-BMA semicontinuous polymerization, monomer feed rates were varied in the range of 0.27–1.10 wt %/min: (A) 0.27, (B) 0.39, (C) 0.55, (D) 0.79, (E) 1.10 in wt %/min.

^b Based on total monomer wt % (80 g). Theoretical solids content: 35.0 wt %; reaction temperature: 25°C.

Physical Properties

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 were used as specimens in the infrared spectroscopy.

Poly (vinylidene chloride) (PVDC) is insoluble in most common solvents at ambient temperature because of its high crystallinity and high melting temperature.^{8,14} Copolymers with a high enough VDC content to be crystalline behave in a manner similar to that of PVDC. In the present study 0.2 g VDC-BMA latex film samples before and after heat treatment at 70°C for 30 min were placed in 3 mL of various common solvents at room temperature and the solubility was observed.

¹³C solid-state NMR spectroscopy was used to examine the difference in sequence distribution of VDC-BMA copolymers. Solid-state NMR experiments were performed using a General Electric NMR Instrument GN-300 spectrometer operating at 75.4 MHz for ¹³C at room temperature. The standard cross-polarization magic angle sample spinning (CP/MASS)¹⁶ 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.

The glass transition temperatures (T_g) and crystalline melting temperatures (T_m) of the VDC-BMA latex copolymers were determined using the DuPont-1090 differential scanning calorimeter. Specimens of 10–20 mg were scanned at a heating rate of 20°C/min. The latexes were dried at room temperature to form films of about 0.1 mm thickness, which were heat treated for 30 min at 70°C before use as specimens. The minimum film-forming temperatures (MFFT) of the VDC-BMA latexes were also determined using MFFT apparatus (Sheen Instrument Co.), which is important for coatings to show sufficient coalescence of the polymer particles to achieve continuity in the film upon drying.

The water vapor transmission rates (WVTR) of the VDC-BMA latex films were determined under the conditions at 72°F and 50% relative humidity by a Honeywell 60 controller under static air conditions. The films were prepared using the photographic paper method.¹⁷ The film thickness was controlled to 1 mil. Glass vials (10 × 60 mm; Kimble

Co.) were used as cells for the water vapor transmission rate study.¹⁸ The weight loss was measured as a function of time. The experiments were continued until the value of the WVTR reached a constant value.

X-ray powder diffraction patterns of PVDC and the VDC-BMA copolymers, heat treated at 70°C for 30 min, were obtained with a Philips automated X-ray powder diffractometer using Ni-filtered CuK α radiation; Scherrer-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 plastic petri dishes pretreated with a mold release agent for epoxy resins (Parafilm, Brice-Driscoll Corp.). These films were used for mechanical characterization after aging at room temperature for 120 days to ensure that the further gradual coalescence and crystallinity were complete. A Rheo-

vibron 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 × 6 × 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. The 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 break was determined from the area under the stress-strain curve. At least three specimens that did not have premature failure were obtained and their average values reported.

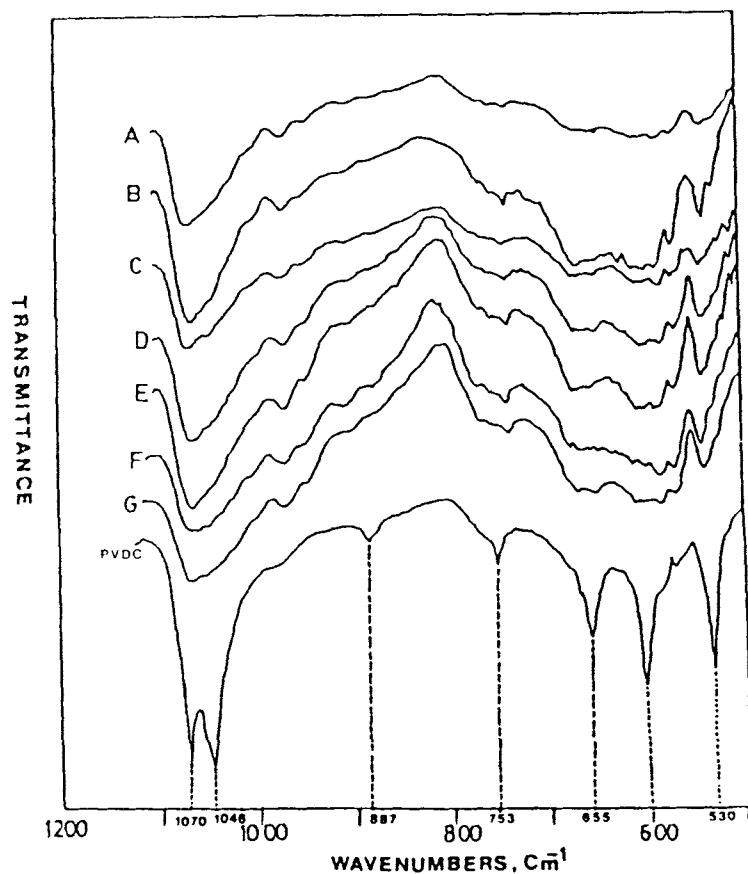


Figure 1 Infrared spectra of 83 : 17 VDC-BMA copolymer latex films A-G, without heat treatment.

RESULTS AND DISCUSSIONS

Physical Properties

For poly(vinylidene chloride) and its copolymers, the infrared bands at 1048, 884, 753, 655, 600, and 530 cm^{-1} are related to the crystallinity of the polymers.¹⁹⁻²² Figures 1 and 2 show the infrared spectra of 83 : 17 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), 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 83 : 17 VDC-BMA copolymer latex films heat treated for 30 min at 70°C showed that, while 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 by seeded batch and batch polymerization did show crystallinity peaks.

These latex films were also aged for 6 months at room temperature. Figure 3 shows the infrared spectra of latex films A, F, and G, respectively, for different aging times. 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 2. Latex film A, prepared by the seeded semicontinuous polymerization with the slowest monomer feed rate, did not show any sign of crystallinity after aging for up to 6 months, indicating that the film was still amorphous in character. However, latex films F and G, by seeded batch and conventional batch polymerization and aged for up to 6 months at room temperature, showed the characteristic crystallinity peaks. It is known^{20,21} that the doublet at 1070 and 1048 cm^{-1} for the crystalline copolymers of vinylidene chloride is replaced by a single peak with the maximum at 1070 cm^{-1} and a shoulder at 1048 cm^{-1} for the amorphous copolymers. The band at 1070 cm^{-1} is stronger than that

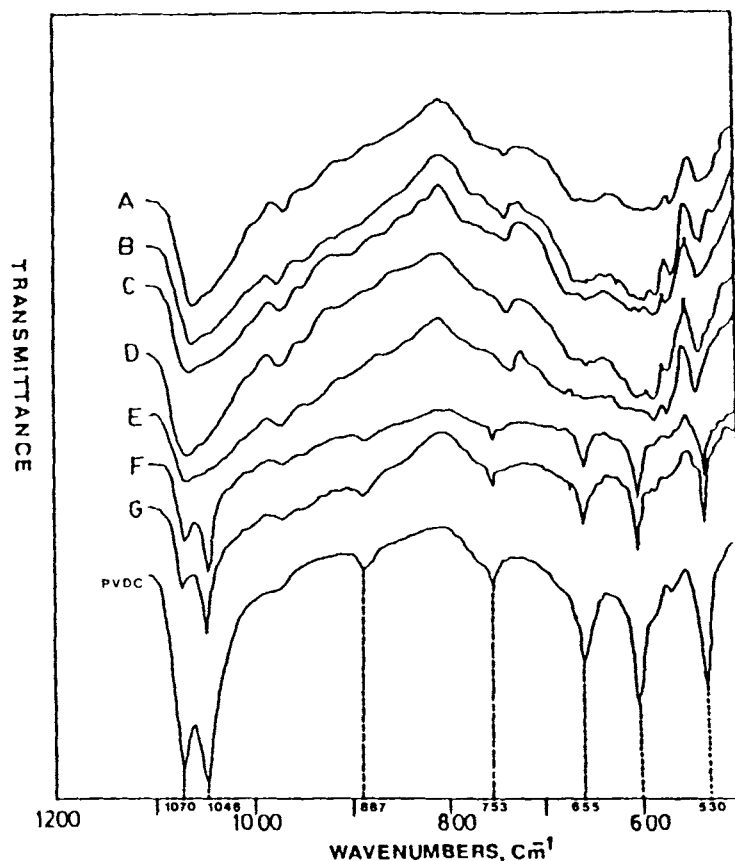


Figure 2 Infrared spectra of 83 : 17 VDC-BMA copolymer latex films A-F, with heat treatment for 30 min at 70°C.

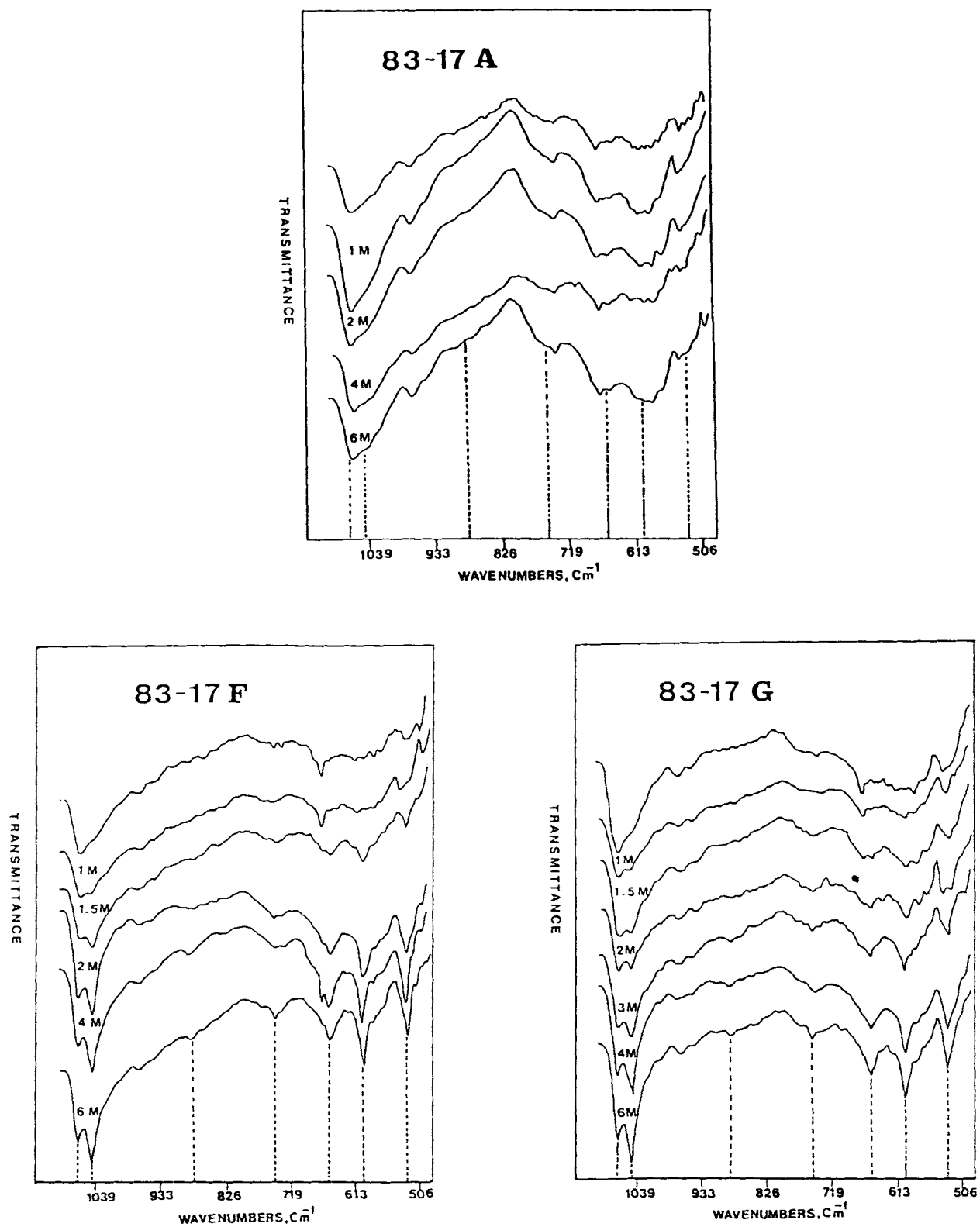


Figure 3 Infrared spectra of 83 : 17 VDC-BMA copolymer latex films A, F, and G, aged for 6 months at room temperature.

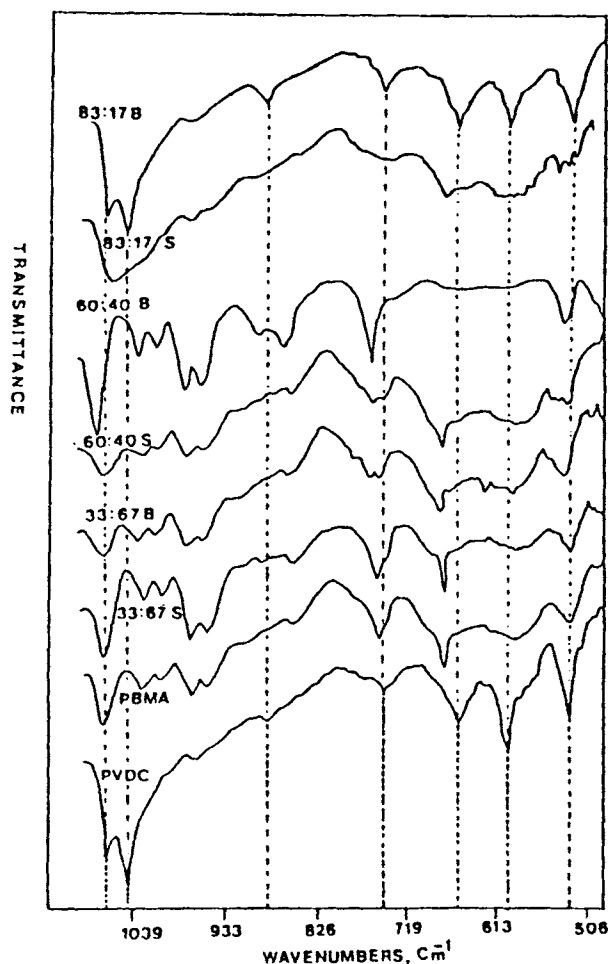


Figure 4 Infrared spectra of VDC-BMA copolymer latex films: (B) batch; (S) semicontinuous polymerization.

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.

Figure 4 shows the infrared spectra of VDC-BMA copolymer latex films prepared by batch and semi-

continuous polymerization, heat treated for 30 min at 70°C . PVDC and 83 : 17 VDC-BMA latex copolymers F and G prepared by batch polymerization showed the characteristic crystalline peaks, whereas none of the other spectra showed these peaks, indicating that all of the VDC-BMA copolymers were amorphous except for the 83 : 17 VDC-BMA copolymers F and G.

A remarkable difference in solubility behavior of VDC-BMA latex films was also found according to the mode of monomer addition and whether they were heat treated. Table II shows the results of the solubility tests of 83 : 17 VDC-BMA copolymer latex films A-G, before and after heat treatment for 30 min at 70°C , carried out at room temperature with various common solvents. Figure 5 also shows a picture of latex films A-G, heat treated for 30 min at 70°C , after dissolution in tetrahydrofuran (THF) at room temperature. Of the latex films heat treated for 30 min at 70°C , latex copolymers F and G, prepared by seeded batch and batch polymerization, were found to be totally insoluble in these common solvents at room temperature. In contrast, for latex films A-E, prepared by seeded semicontinuous polymerization, the solubility varied from totally soluble to partially insoluble with increasing monomer addition rate (R_a). The freshly made latex films A-G without heat treatment were found to be more soluble than those after heat treatment, as shown in Table II. These results indicate that the solubility is very sensitive to the crystallinity of these latex films.

Figure 6 shows the solubility behavior of the VDC-BMA copolymer latex films in THF. All of the latex films, prepared by seeded semicontinuous polymerization, were found to be completely soluble in THF, irrespective of the monomer composition, indicating that the copolymers were amorphous and the copolymer composition homogeneous. In contrast, the latex films, prepared by batch polymerization, showed different behavior depending on the monomer composition. The amount of insoluble polymer increased with increasing VDC content, indicating an increase in the degree of crystallinity and a more heterogeneous copolymer composition. The solubility of the latex films varied inversely with their crystallinity.

^{13}C solid-state NMR spectroscopy was used to examine the difference in sequence distributions of VDC-BMA copolymer, prepared by batch and semicontinuous processes. The 83 : 17 VDC-BMA copolymers prepared by batch polymerization did not dissolve in any of the solvents at room temperature. At temperatures above 130°C , however, it did

Table II Solubility of 83 : 17 VDC-BMA Copolymer Latex Films

Sample ^a	Dioxane	MEK	DMF	MC	NB	TOL	THF	NMP
Without Heat Treatment								
A	S	S	S	S	S	S	S	S
B								
C								
D								
E								
F	PS	IS	PS	IS	IS	IS	PS	PS
G	PS	IS	PS	IS	IS	IS	PS	PS
With Heat Treatment								
A	S	PS	S	PS	S	PS	S	S
B	S	PS	S	PS	—	PS	S	S
C	S	PS	S	PS	—	PS	S	S
D	S	PS	PS	PS	—	PS	PS	S
E	PS	PS	PS	PS	—	PS	PS	S
F	IS	IS	IS	IS	IS	IS	IS	IS
G	IS	IS	IS	IS	IS	IS	IS	IS

^a 0.2 g polymer in 3 mL solvent at room temperature; S soluble; PS partially soluble; IS insoluble. MEK methyl ethyl ketone; DMF dimethyl formamide; MC methylene chloride; NB nitrobenzene; TOL toluene; THF tetrahydrofuran; NMP *N*-methyl pyrrolidinone.

dissolve in nitrobenzene, with serious degradation and discoloration, and the evolution of hydrochloric acid.

Figure 7 shows the ¹³C solid-state NMR spectra of deuterated benzene-swollen or dissolved 83 : 17

VDC-BMA copolymers prepared by batch and semicontinuous polymerization, respectively, using the cross-polarization (CP) technique.¹⁶ The batch sample showed two strong peaks at 64 and 87 ppm, which represent PVDC, and four small peaks at 15,

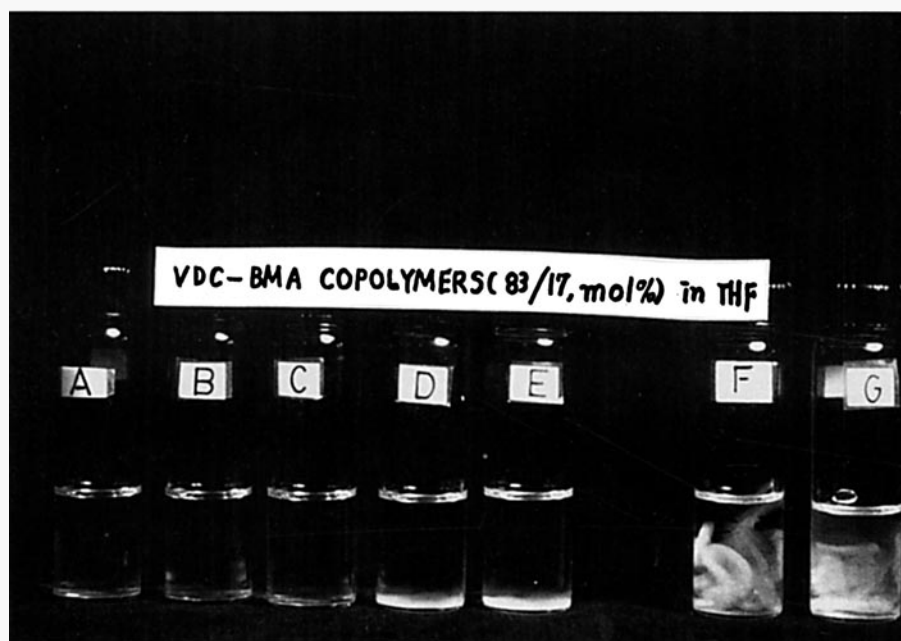
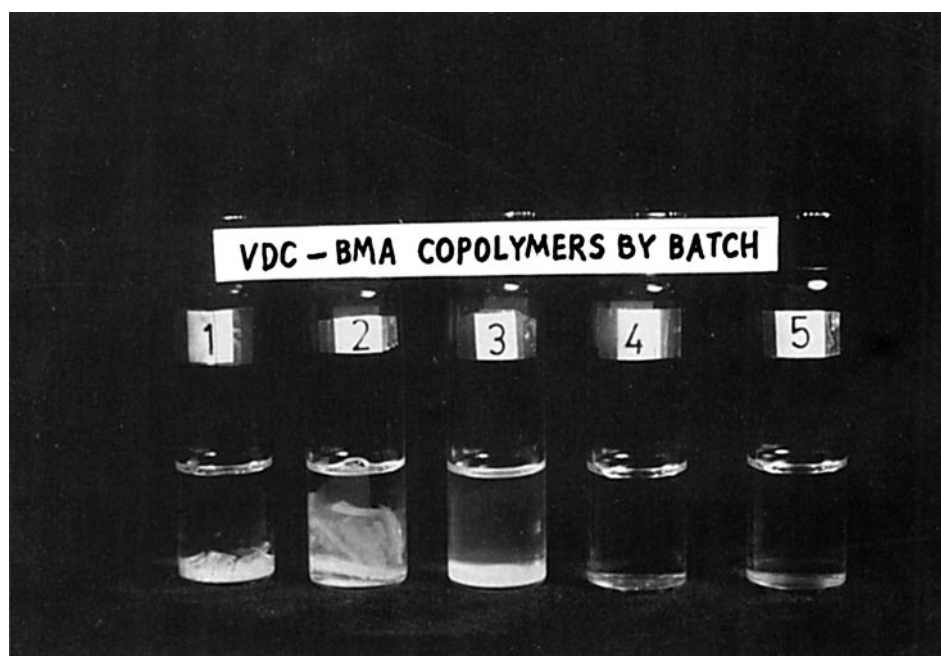
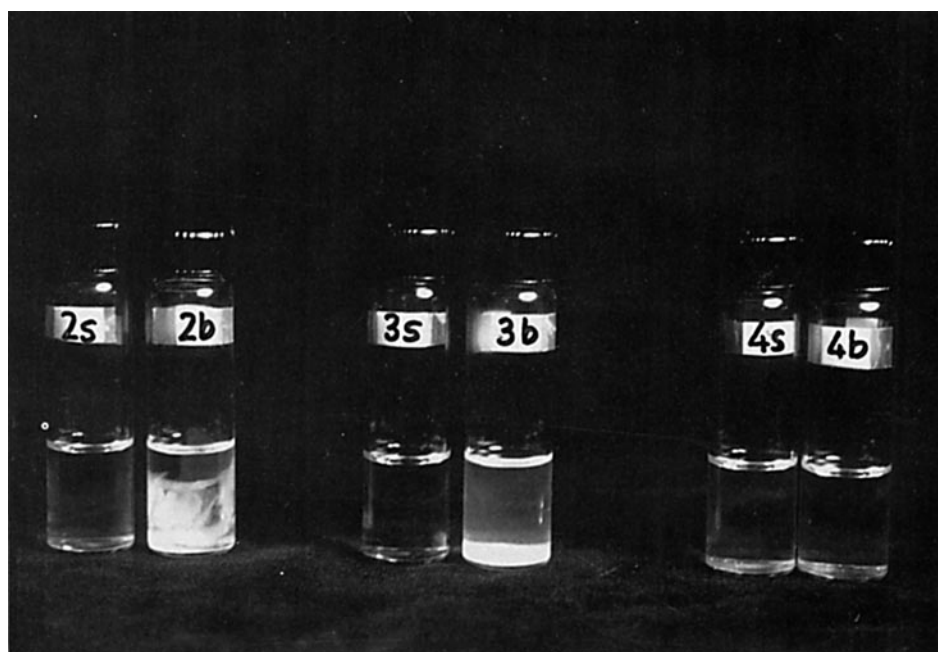


Figure 5 Solubility of 83 : 17 VDC-BMA copolymer latex films in THF.



(1) PVDC, (2) 83:17, (3) 60:40, (4) 33:67,
(5) PBMA.



b: batch process

s: semicontinuous process

Figure 6 Solubility in THF of VDC-BMA copolymer latex films.

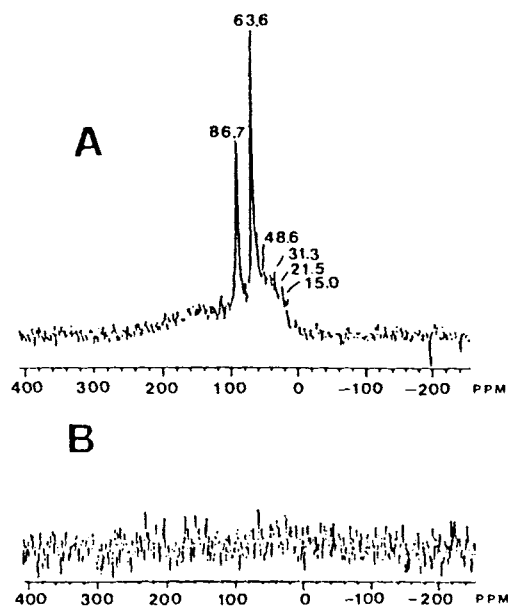


Figure 7 ^{13}C solid-state NMR spectra of deuterated benzene-swollen or dissolved 83 : 17 VDC-BMA copolymers, prepared by (A) batch and (B) semicontinuous polymerization using the cross-polarization technique.

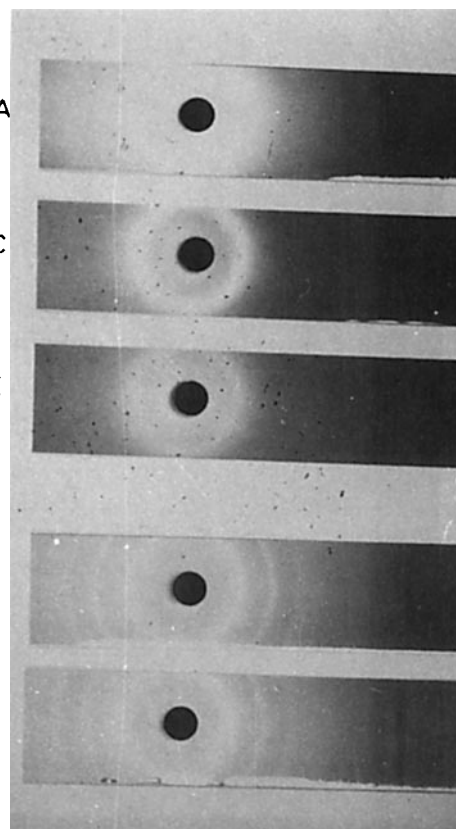
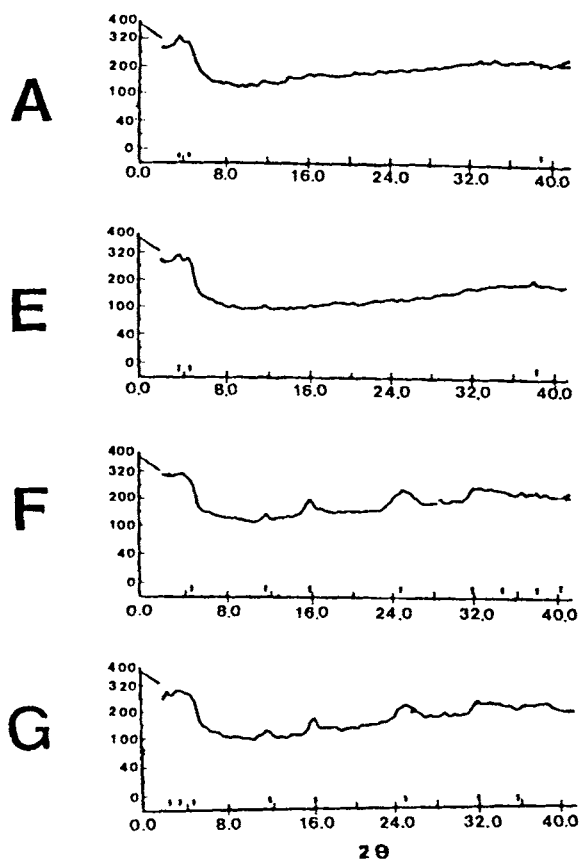


Figure 8 X-ray diffraction patterns and Scherrer-Debye ring patterns of 83 : 17 VDC-BMA copolymer latex films, heat treated for 30 min at 70°C .

21.5, 31.3, and 48.6 ppm, which arise from Poly(butyl methacrylate) (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 cross-polarization technique, indicating the sample was amorphous. It is intrinsically difficult to obtain quantitative information from cross-polarization NMR spectra of systems with significant motion. However, the differences between the spectra of the batch and semicontinuous samples suggest that the batch sample had much less molecular motion due to the presence of the crystallites.

Figure 8 shows the X-ray diffraction patterns and Scherrer-Debye ring patterns of the 83 : 17 VDC-BMA copolymer latex films heat treated for 30 min at 70°C . Latex films F and G showed the same diffraction peaks and same 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,

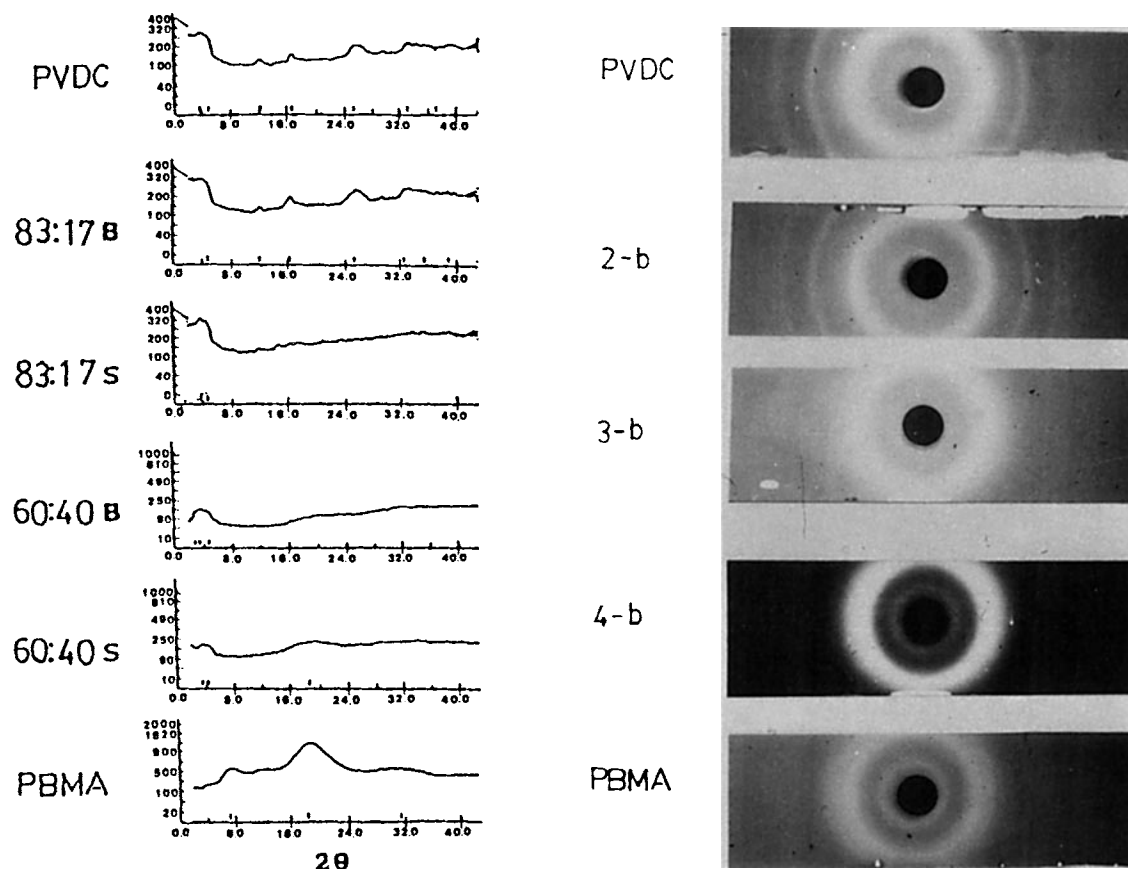


Figure 9 X-ray diffraction patterns and Scherrer-Debye ring patterns of VDC-BMA latex films, heat treated for 30 min at 70°C: (2-b) 83 : 17, batch; (3-b) 60 : 40, batch; (4-b) 33 : 67, batch.

did not show any characteristic crystalline peaks or regular ring patterns, indicating that these polymers are amorphous in character. Figure 9 shows the X-ray diffraction patterns and Scherrer-Debye ring patterns of VDC-BMA copolymer latex films prepared by both batch and semicontinuous polymerization and heat treated for 30 min at 70°C. PVDC and the 83 : 17 VDC-BMA copolymers F and G, prepared by batch polymerization, showed diffraction peaks and regular ring patterns characteristic of crystallinity. However, none of the other copolymers showed peaks or regular ring patterns, indicating that these copolymers were amorphous in

Table III WVTR Values of VDC-BMA Copolymer Latex Films $\times 10^8$ (g mil/cm² min)

83 : 17		60 : 40		33 : 67		PBMA
S	B	S	B	S	B	
19.6	1.6	143.0	91.9	335.0	177.0	350.0

character. These results are consistent with those of the infrared spectroscopy.

Table III shows the values of the WVTR of VDC-BMA copolymer latex films, prepared by both batch and semicontinuous polymerization, heat treated for 30 min at 70°C. In general, the value of the WVTR decreased with increasing amount of VDC in the copolymer, and the values of the WVTR of the latex films prepared by batch polymerization were smaller

Table IV T_g , T_m , and MFFT Values for 83 : 17 VDC-BMA Copolymer Latex Films^a

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

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

Table V T_g , T_m , and MFFT Values of VDC-BMA Copolymer Latex Films^a

°C	PVDC	83 : 17		60 : 40		33 : 67		PBMA
		S	B	S	B	S	B	
T_g^b	5.9	16.3	24.2	33.0	32.0	39.2	38.8	38.1
T_g^c	—	30.9	41.3	46.0	44.3	54.4	54.9	47.5
MFFT	—	+	+	23.9	24.9	33.6	33.3	34.1
T_m^b	199.0	=	187.0	=	=	=	=	=

^a +, lower than 5°C; =, no T_m observed; S semicontinuous process; B batch process.

^b Determined by DSC; heating rate 20°C/min.

^c Determined by Rheovibron at 110 Hz.

than those of their semicontinuous counterparts. Especially, a considerable difference was found in the values of WVTR of latex films A and G, prepared by semicontinuous polymerization with the slowest monomer feed rate and by batch polymerization, respectively. Latex film G had a WVTR value about 12 times lower than latex film A. These results indicate that the presence of crystallites in latex films prepared by batch polymerization improved the barrier properties by acting as a nonporous filler in the composite system.^{23,24}

Thermal Properties

Table IV shows the glass transition temperature (T_g) and the crystalline melting temperature (T_m) determined by DSC (heating rate; 20°C/min) for the 83 : 17 VDC-BMA latex films heat treated for 30 min at 70°C, and their minimum film-forming temperature (MFFT) values. All the latexes were good film forming at room temperature. 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 respectively, by the seeded batch and batch polymerization, showed T_g values 7-8°C higher than those for the copolymers prepared by semicontinuous polymerization. Only latex films F and G, prepared by batch polymerization, showed crystalline melting temperatures of 184 and 187°C, respectively. Also, the difference in melting temperatures between latex films F and G might be due to the difference in size of the crystallites present in the 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 polymerizations, 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 latex films F and G, prepared by batch polymerization, have T_g values 7-8°C higher than those of latex films A-E, prepared by seeded semicontinuous polymerization, might be due to the presence of crystallites in batch copolymers, which reduce the mobility of amorphous chains trapped between crystallites, thereby increasing the T_g .^{23,24} It should be also noted that, for latexes F and G, prepared by batch polymerization, which are film forming at room temperature with amorphous character, the corresponding latex films heat treated for

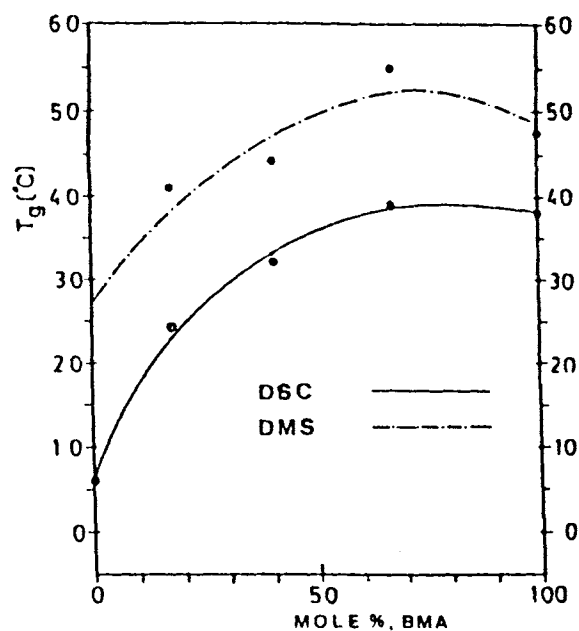


Figure 10 Variation of T_g with composition of VDC-BMA batch copolymers.

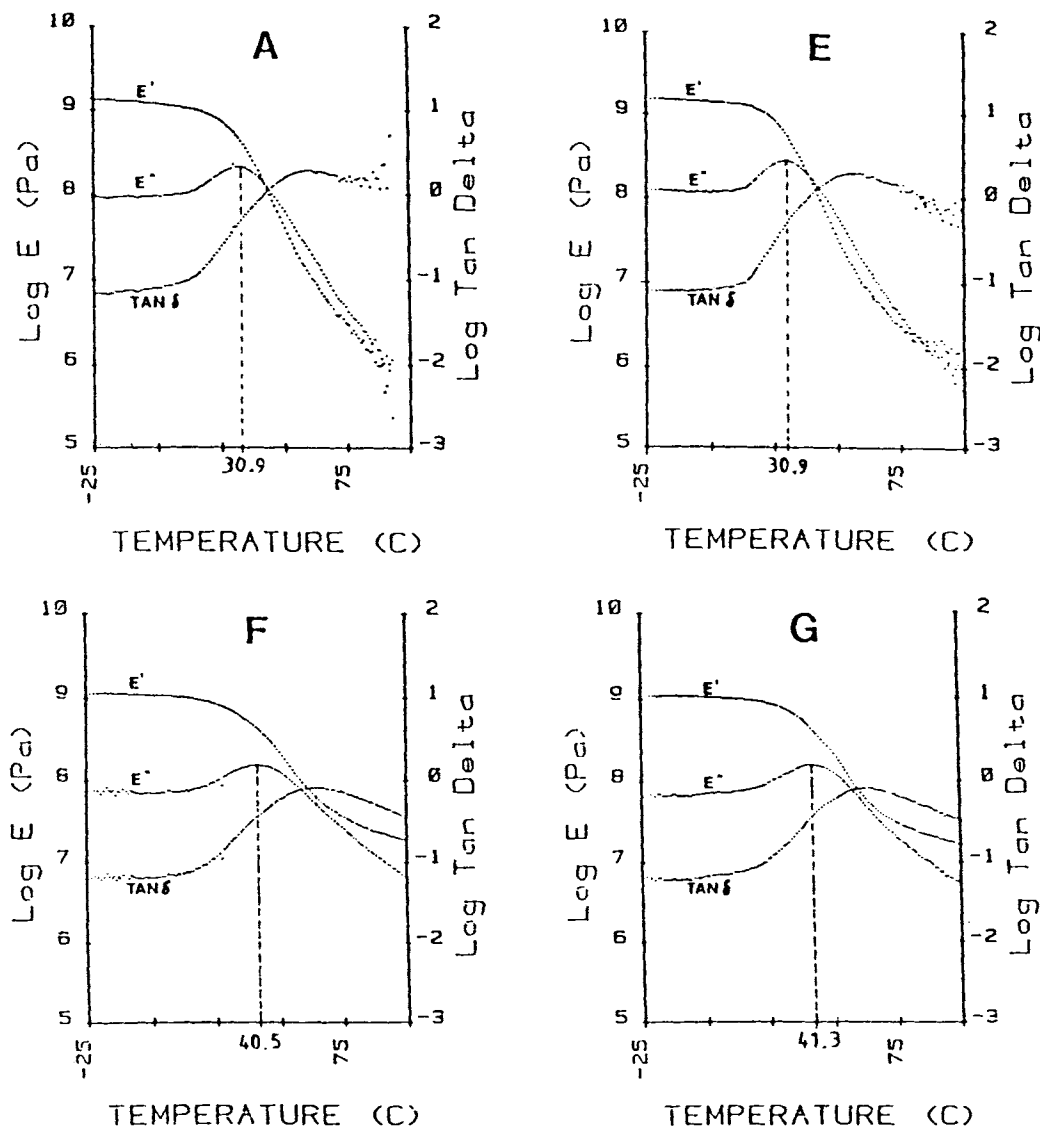


Figure 11 Dynamic mechanical spectra of 83 : 17 VDC-BMA copolymers A-G, prepared by semicontinuous and batch processes.

30 min at 70°C or aged for up to several months 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.

Table V shows the T_g and T_m of VDC-BMA copolymer latex films prepared by both batch and semicontinuous polymerization, heat treated for 30 min at 70°C. The difference in T_g between copolymers, prepared by batch and semicontinuous polymerization, decreased with increasing amount of BMA, i.e., 8–9°C for the 83 : 17, 1–2°C for the 60 : 40, and 0–1°C for the 33 : 67 VDC-BMA copolymers, indicating differences in their sequence distributions. It was found that these VDC-BMA copoly-

mers, prepared by batch polymerization have a T_g maximum at around 39.0°C for the 30 : 70 VDC-BMA copolymer, as shown in Figure 10. Many investigators reported a pronounced T_g maximum and T_g minimum in VDC copolymer systems.²⁵⁻³⁰ The cause of the T_g maximum in VDC-BMA copolymer systems is not yet clear. More work should be done on this subject.

Mechanical Properties

Figure 11 shows the results for dynamic mechanical analysis for the 83 : 17 VDC-BMA latex films using the Rheovibron viscoelastomer at 110 Hz and a heating rate of 1°C/min. Latex films A-E, prepared

by seeded semicontinuous polymerization, showed almost the same 30–31°C T_g value. In contrast, 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 that 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 latex films A–E, prepared by semicontinuous polymerization, however, were narrower than those of latex films F and G, prepared by batch polymerization, respectively, indicating again that the copolymers prepared by the semicontinuous polymerization have more homogeneous copolymer compositions than their corresponding counterparts. The storage modulus E' in 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 in latex films F and G, prepared by seeded batch and batch polymerization, respectively, approached a value of $10^{7.2-7.3}$ Pa at 100°C with non-scattered data points, indicating that latex copolymers F and G have higher moduli at the rubbery plateau region. 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 characteristic peaks in the infrared spectra and X-ray diffraction patterns. The crystallites in crystalline material may act as a reinforcing filler or crosslinker between the amorphous regions, and increase the modulus and the stiffness in the composites.^{23,24} This may be why copolymers F and G have higher moduli and more hardness than their corresponding counterparts at rubbery plateau region.

Significant differences were also found in tensile properties of the VDC–BMA latex films. Table VI 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. It was found that the latex films prepared by semicontinuous polymerization were flexible and tough, while the latex films prepared by batch polymerization were hard and brittle, which can be explained by the presence of the crystallites acting as reinforcing fillers or crosslinkers in the copolymers.^{23,24} The tensile properties of latex films A–E, prepared by semicontinuous polymerization, varied also with the monomer addition rate used in the polymerizations. Young's modulus and ultimate strength increased, and the percent elongation and toughness decreased with increasing monomer addition rate (R_a). This result indicates that, even in semicontinuous polymerization, the unit length of VDC molecule in copolymers is controlled by the monomer feed rate. This result correlates with the result of solubility in various solvents as shown in Table II. Table VII shows the results of tensile properties for the VDC–BMA copolymer latex films. For the 60 : 40 VDC–BMA copolymer latex films prepared by both batch and semicontinuous polymerization, the tensile properties were found to be similar, irrespective of the polymerization process. However, for the 33 : 67 VDC–BMA copolymer latex films, batch latex film showed higher modulus, lower percent elongation, and lower energies to break, resembling PBMA.

CONCLUSIONS

The method of monomer addition as well as the monomer composition are found to have a considerable effect on the physical and mechanical properties of VDC–BMA copolymer latex films. The VDC–BMA copolymer latex films, prepared by monomer-starved semicontinuous polymerization, were much more homogeneous in composition, amorphous in character, lower T_g values, and lower ultimate strength and higher elongation percent to

Table VI 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, $\sigma\mu^b$ (MPa)	1.3	2.7	2.7	2.9	2.9	7.6	8.4
Elongation to break, $\chi\mu$ (%)	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.

Table VII Tensile Properties of VDC-BMA Copolymer Latex Films^a

Samples	83 : 17		60 : 40		33 : 67		PBMA
	S ^b	B	S ^b	B	S ^b	B	
Young's modulus, $E^{c,d}$ (MPa)	3.4	296.3	274.2	294.2	314.2	359.0	370.7
Ultimate strength, $\sigma\mu^d$ (MPa)	1.3	8.4	19.3	20.2	24.5	13.6	13.7
Elongation to break, $\chi\mu$ (%)	588	87	228	234	91	42	6
Energy to break, τ^d (MJ/m ³)	15.6	6.1	32.8	34.4	11.5	3.1	0.4

^a S = semicontinuous process, B = batch process.

^b Monomer feed rate: 0.27 wt %/min.

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

^d Based on the initial cross-sectional area.

break, compared to corresponding copolymer films by batch polymerization. On the other hand, the VDC-BMA copolymer latex films, prepared by batch polymerization where the composition drifts took place with conversion, were much more heterogeneous composition, crystalline in character, lower WVTR values, and higher ultimate strength and lower elongation percent to break, compared to their corresponding counterparts. These differences in physical and mechanical properties indicate that the unit length of VDC molecule in copolymers was controlled by the monomer feed rate in semicontinuous polymerizations.

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