# Melting Behavior and Surface Morphology of Poly(vinyl acetate-*co*-vinyl alcohol) Copolymer

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Received 26 September 2001; accepted 24 January 2002

**ABSTRACT:** In a study of the surface morphology of commercial poly(vinyl acetate-*co*-vinyl alcohol) (ACA copolymer) with different percents of hydrolysis, different structures like fibrils, spherulites, micelles, vesicles, and spheroids were seen. The copolymer was crystallized by annealing at two different temperatures. The morphology of the polymer after crystallization and also without crystallization was studied. A decrease in the melting temperature just by heating to the melting temperature was observed, and for a detailed study, repetitive heating of the copolymer was carried out and changes in the mass and heat of fusion after every heating was recorded. The morphology of the copolymer after repetitive heating was studied. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1211–1218, 2002

**Key words:** poly(vinyl acetate-*co*-vinyl alcohol); spherulites; vesicles; lamellae; annealing; melt; crystallization

## INTRODUCTION

Block copolymers self-assemble in selective solvents. They form micelles in bulk consisting of an inner core composed of solely insoluble segments and an outer shell of soluble segments swollen by the solvent. Depending on the composition of the block copolymers, the micelles can be distinguished into two types: star and crew cut. There is no sharp boundary between the two classes of aggregates. The former is usually made from a block copolymer in which corona-forming blocks are longer than are the core-forming blocks, while the latter is made from a copolymer in which the core-forming blocks are much longer.[1] The thermal analytical technique has been widely used to characterize the comonomer sequence distribution in the poly(vinyl acetate–*co*–vinyl alcohol) (ACA) copolymer.[2,3] The micelle formation in ACA copolymers was observed by thermogravimetric and X-ray analyses.[3]

Amphiphilic copolymers are an important material in the fields of natural science and biochemistry as well as in the industrial field. They have a variety of applications, such as in emulsifiers, colloid stabilizers, and drug-delivery systems. The ACA copolymer has a very large number of industrial applications including use as a protective colloid in emulsion and suspension. The ACA copolymer can be prepared by hydrolysis or saponification of poly(vinyl acetate) (PVAC) and by reacetylation of poly(vinyl alcohol) (PVA).[4,5] The total degree of hydrolysis and sequence distribution of monomer units in the copolymer regulate the properties of these copolymers, such as the degree of crystallinity and the melting temperature. The copolymer composition, sequence length, and block character of residual vinyl acetate units that affect mainly the structure–property relationship can be quantitatively measured by $^{13}$C-NMR spectroscopy.[6]

In this article, different morphologies of the ACA copolymer at the equilibrium melting temperature, after a standard thermal history and also without it, are discussed in the Results and Discussion section. A continuous decrease in the melting temperature of the copolymer, regardless of the vinyl acetate and vinyl alcohol content in the copolymer, was observed and the morphologies after repetitive heating to the melting temperature were studied.

## EXPERIMENTAL

ACA with different percents of hydrolysis, such as A = 97–99%, B = 87–89, C = 97–98%, and D = 94–96%, from Poly Chem. India (Mumbai, India) were use for the study.

### DSC analysis

The melting temperature of the polymer is dependent on several experimental factors: One of the factors is the rate at which the polymer is heated and another is the thermal history of the sample. All the samples were crystallized by annealing at two different temperatures, 120 and 160°C, after heating to 320°C and holding this temperature for 10 min to establish the

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Journal of Applied Polymer Science, Vol. 86, 1211–1218 (2002)

**TABLE I**
**Melting Temperature, Heat of Fusion, and Mass After Repetitive Heating**

| No. times heated | Melting temperature (°C) | Heat of fusion (J/g) | Weight of the sample after crimping in the pan (g) |
|---|---|---|---|
| 1 | 230.1 | 80.42 | 0.032803276 |
| 2 | 227.7 | 69.85 | 0.032400038 |
| 3 | 227.1 | 66.77 | 0.032403237 |
| 4 | 224.3 | 62.46 | 0.032203225 |
| 5 | 224.5 | 58.45 | 0.032203218 |
| 6 | 223.7 | 58.37 | 0.032103208 |
| 7 | 223.6 | 52.89 | 0.032103207 |
| 8 | 221.5 | 53.24 | 0.032003203 |
| 9 | 221.5 | 47.06 | 0.031903187 |
| 10 | 218.8 | 46.79 | 0.031803180 |
| 11 | 217.9 | 43.71 | 0.031703175 |

Net weight of the sample taken in a pan was 8.2 mg. These values were noted for 97–99% hydrolyzed ACA copolymer.

standard thermal history. Sample A was heated to the melting temperature and cooled to room temperature; this procedure was carried out several times to observe the changes in the $T_m$ and the heat of fusion. For repetitive heating, after taking the neat weight of the polymer, the pan was weighed after crimping along with the sample. After each heating, the weight of the pan was recorded, which is given in the Table I. The equilibrium melting temperature was obtained in our earlier work.[3] Differential scanning calorimeter (DSC) data were obtained using a Perkin–Elmer DSC-7 equipped with a thermal analysis data station. A polymer sample was run in aluminum pans with a sample weight of 8–12 mg under a nitrogen atmosphere. Instrument calibration was done using the indium standard. After observing the rate of heating on the $T_m$, all the samples were run at 20ºC $\text{min}^{-1}$. All the samples were heated repeatedly, that is, a sample was heated to the melting temperature and then cooled to room temperature at a rate of 320ºC $\text{min}^{-1}$ in all the cases except for annealing. The repetitive heating was carried out for 20 times; the change in the mass and heat of fusion was recorded by heating 10 times.

### SEM analysis

The morphology of all the samples was studied after and before crystallization of the copolymer. SEM analysis was done by using a Leica Cambridge (Stereoscan 440) scanning electron microscope (Cambridge, 5000, UK). A polymer specimen was coated with gold in an automatic sputter coater (Polaron Equipment Ltd., scanning electron microscope coating unit E 5000, UK). Photographs of representative areas of the sample were taken at different magnifications.

## RESULTS AND DISCUSSION

Block copolymers composed of crystalline and amorphous blocks are interesting materials to study the crystal structure, morphology, crystallization kinetics, and dynamics. Microphase separation in the semicrystalline block copolymer was observed either by block incompatibility or by crystallization of one or more blocks. Prior work on the ethylene b (ethylene-*alt*-propylene) system (E/EP) demonstrated that, when the block incompatibility is small, crystallization proceeds from single-phase melt and alternating lamellae microdomains result regardless of the copolymer composition.[7]

The melting temperatures provided by DSC analysis were used to estimate the blockiness of the ACA copolymer using the theories of Flory[8] or Baur.[9] Thermal analysis is a more convenient tool experimentally and can provide accurate results, provided that the melting temperature ($T_m$) is consistent after annealing.

Flory related the melting point, $T'_m$, of a copolymer to the homopolymer of the crystallizable monomer $T'_m$ by

$$(1/T_m) - (1/T'_m) = -(R/\Delta H\mu) \ln P_{\mathrm{OH,OH}} \quad (1)$$

where $R$ is the gas constant; $\Delta H\mu$, the molar enthalpy of fusion per crystallizable monomer unit; and $P_{\mathrm{OH,OH}}$, the probability that a crystallizable group (vinyl alcohol) was joined to another like group. For a random copolymer, $P_{\mathrm{OH,OH}}$ = the mol fraction of crystallizable units = (OH), the alternating copolymer of $P_{\mathrm{OH,OH}} <$ (OH). Baur's theory yields the expression

$$(1/T_m) - (1/T'_m) = -(R/\Delta H\mu) \times \{\ln P_{\mathrm{OH,OH}} - 2\,[1 - P_{\mathrm{OH,OH}}](\mathrm{OH})\} \quad (2)$$

Flory assumed that longer sequences of crystallizable monomer residues crystallize at higher temperatures than do shorter sequences. Baur's model postulates that every sequence length can be found in the amorphous as well as in the crystalline regions of the solid polymer.

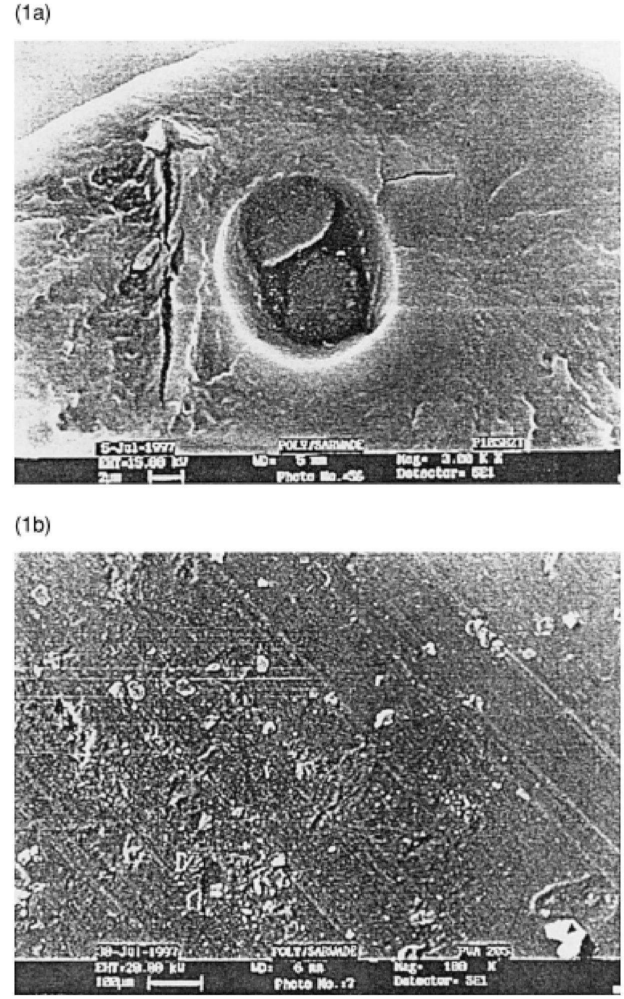

**Figure 1** (1a,b) Morphology of sample A, 97–99%, and B, 87–89% hydrolyzed. Samples were analyzed without crystallization.

The sequence probability of noncrystallizable units, $P_{\mathrm{OAC,OAC}}$, can be defined[10] as

$$P_{\mathrm{OAC,OAC}} = 1 - [(\mathrm{OH})\,(1 - P_{\mathrm{OH,OH}})/(\mathrm{OAC})] \quad (3)$$

Note that (OH) + (OAC) = 1, but $P_{\mathrm{OH,OH}} + P_{\mathrm{OAC,OAC}}$ is not necessarily equal to 1). It is possible to determine the number-average sequence length $L_{\mathrm{OH}}$ by[11]

$$L_{\mathrm{OH}} = (1 - P_{\mathrm{OH,OH}})^{-1} \quad (4)$$

Similarly, the blockiness factor, $\eta$, is defined as

$$\eta = (1 - P_{\mathrm{OH,OH}}) + (1 - P_{\mathrm{OAC,OAC}}) \quad (5)$$

Equations (3) and (5) hold for both theories.

In our earlier work, the constant crystallization temperatures of polymer samples were determined by DSC. Subsequently, DSC results were analyzed by Flory's and Baur's theories and then compared with the NMR data.[3]

In the morphology studied after taking the equilibrium melting temperature, the establishment of an ordered melt morphology is an added complexity for semicrystalline block copolymers. With an increase in the block incompatibility, microphase separation may occur in the melt prior to crystallization. The presence of melt microdomains affects the crystallization process and the resultant morphology.[12–21]

The copolymer is of technological importance because covalent linkage prevents macrophase separation. Theoretical treatment of block copolymer microstructures were first developed for two limiting regimes, designated strong and weak segregation depending on whether or not the enthalpic terms dominate the free energy. A wider variety of chemical structures in both weak and intermediate segregation regimes were reported with intriguing results.[22]

The morphology of the polymers without crystallization or without a standard thermal history are shown in Figures 1(1a,b) and 2(1c,d) for samples A, B, C, and D, respectively. Lamellae with disorders de-

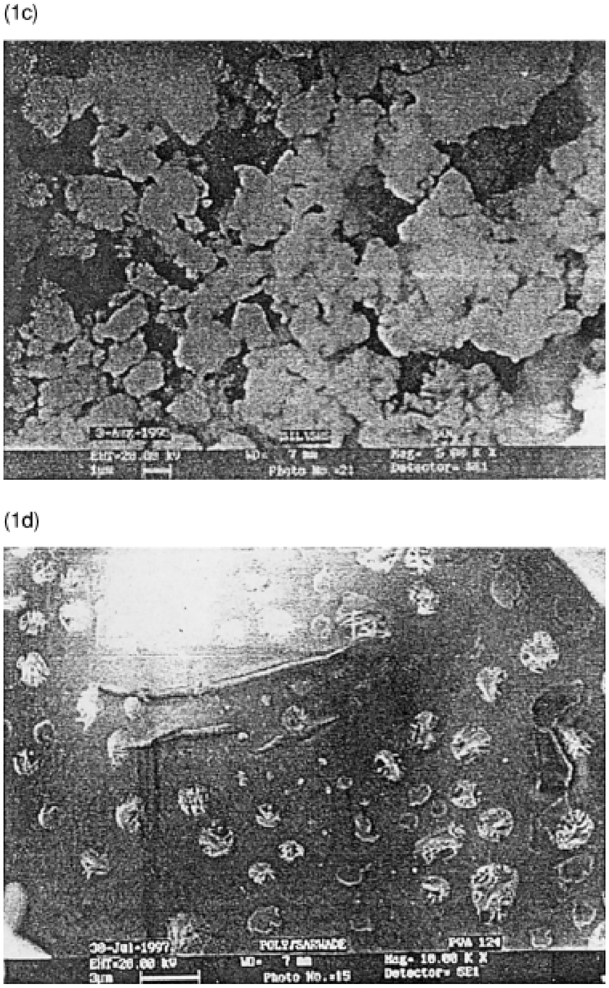

**Figure 2** (1c,d) Morphology of C, 97–98%, and D, 94–96% hydrolyzed. Samples were analyzed just after heating to the melting temperature.

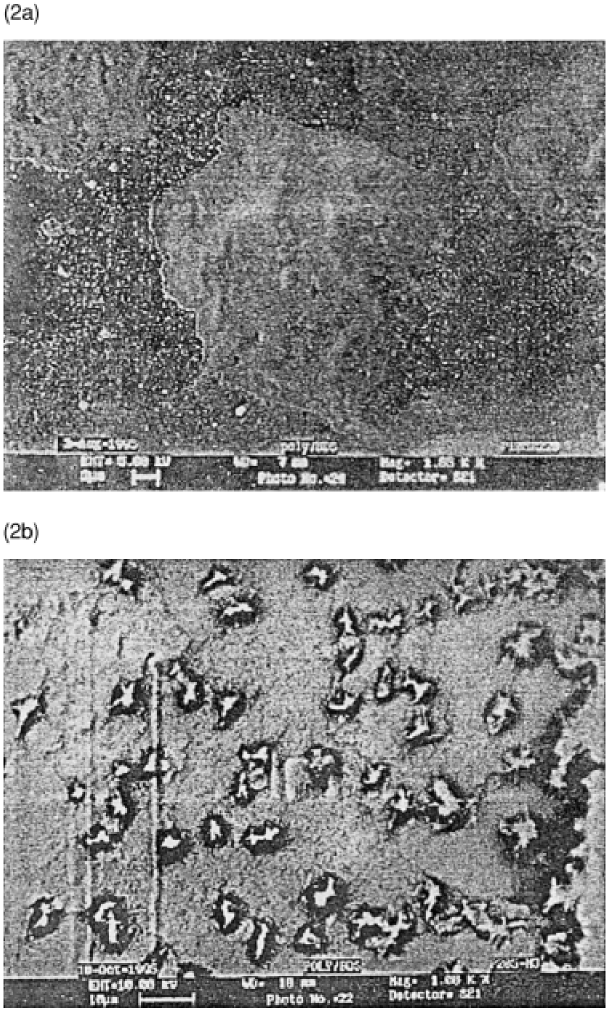

**Figure 3** (2a,b) Morphology of samples A and B after crystallization by annealing at 120ºC. Spherulites in 2a and developing spherulites in 2b can be seen.

pending on the thermal history of the polymer can be seen. Figures 3(2a,b) and 4(2c,d) show the morphology after the equilibrium melting temperature. Lamellae, developing spherulites, and vesicles were observed in samples A, B, C, and D by annealing at 120ºC. Big vesicles, broken vesicles, and fibrillar structures were observed by annealing at 160ºC, shown in Figures 5(3a,b) and 6(3c,d). Repetitive heating for 2, 10, 11, and 20 times resulted in different morphological structures, such as fringed micelles, developing spherulites, lamellae, and vesicles, which can be seen in Figures 7(4a,b) and 8(4c,d). Figure 9 shows a decrease of the melting temperature after repetitive heating.

The different meanings attached by various authors to the term micelle has given rise to a great deal of confusion in some branches of colloid science. The word micelle has been used for any polymolecular-dispersed colloid particles of a crystalline nature, that is, crystalline particles of a colloidal dimension no matter if dispersed in a solution or if occurring in a coherent solid system. The conditions given below must be fulfilled in order that a gel can be formed from a solution: (1) A solid substance should separate from the solution in a finely dispersed colloidal state. (2) The separated solid particles should neither be deposited by gravity nor remain in the colloidal suspensions' freely moving kinetic units, but they should join together to form a continuous coherent framework throughout the mass of the solution from any process, virtually capable of producing the separation of some solid phase either crystalline or amorphous, from a solution or melt, or gel or micelle formation may result. The condition of supersaturating is caused either by a change of temperature, by evaporation, by addition of another substance, or by a chemical reaction that occurs at a first step, secondary formation of a continuous pattern, or a framework of colloidal fineness.[23]

In the case of the ACA copolymer supersaturating along with the change in temperature with evaporation may lead to the formation of a continuous coher-

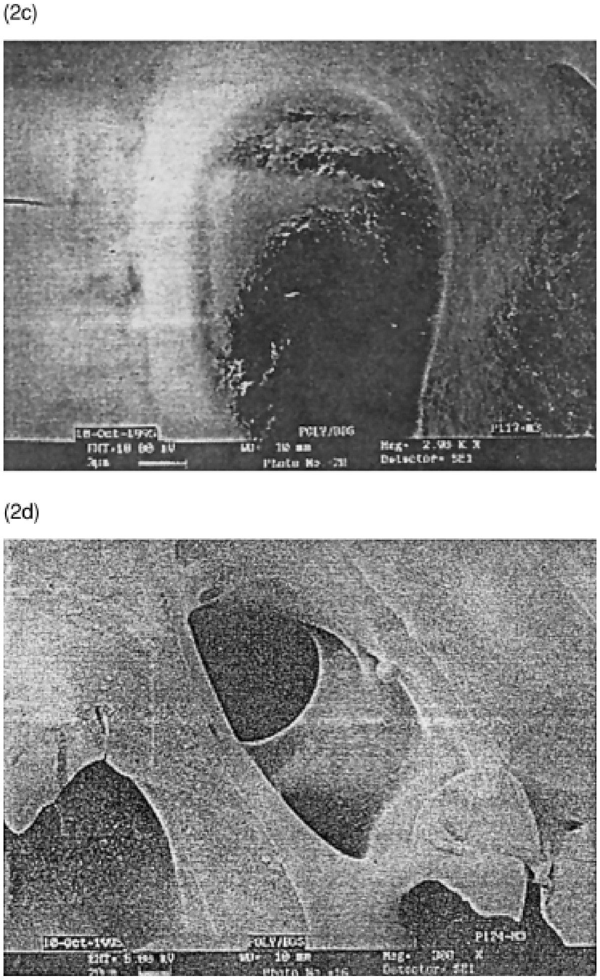

**Figure 4** (2c,d) Morphology of samples C and D after crystallizing at 120ºC. Lamellae, vesicles, and broken vesicles can be seen in 2c and 2d.

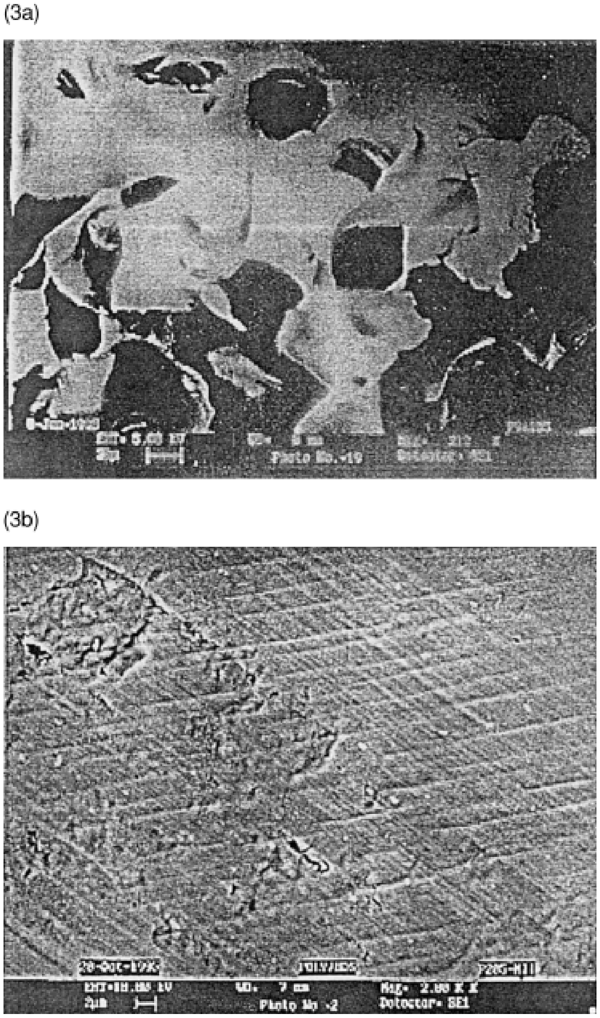

**Figure 5** (3a,b) Morphology of samples A and B after crystallizing at 160ºC. Broken vesicles can be seen in 3a, while disorder can be seen in the crystalline structure of 3b.

ent gel-like structure or big vesicles which can be seen in the morphology of an annealed sample. One can see the disorder in the structure and different morphological structures, such as fibrils, spherulites, and spheroids, for the sample, without a standard thermal history, which were not crystallized, as shown in Figures 1(1a,b) and 2(1c,d). Lamellae with a structure disorder depending on the thermal history can be seen in Figure 1(1a). Broken vesicles are seen in samples annealed at 160°C. Also, the sample with 20 times of repetitive heating showed broken vesicles [Fig. 8(4d)], whereas the sample with 11 times of repetitive heating showed lamella with broken vesicles [Fig. 8(4c)]. In the morphology, just after two or 10 times of repetitive heating, lamellae with chain folding and radial growth of lamellae can be seen.

There is much more appreciation of the variety of morphological forms exhibited by lamellar crystals in melt-grown polyethylene.[24,25] The kinetic theory of polymer crystallization with chain folding has had considerable success in the understanding and interpreting of the data on melt-crystallized linear polymers. In the kinetic nucleation theory of polymer crystallization in regime I, which occurs nearest to the melting point, the observable growth rate $G$ is proportional to the surface nucleation rate $i$, while in the lower-temperature regime II, it is proportional to $i^{1/2}$. The shape of the spherulite or oxialite and the molecular weight can be interpreted in quantitative terms, and the values of the fold surface free energy and the work of chain folding can be derived from these kinetic measurements, which are in reasonable accord with independent theoretical and experimental determination of these quantities.[24–30]

The net weight of the sample taken in a pan is equal to 8.2 mg. These values were noted for a 97–99% hydrolyzed ACA copolymer.

It is known that the crystallinity and melting point of the ACA copolymer varies with the distribution of the residual acetyl groups. The lower the crystallinity

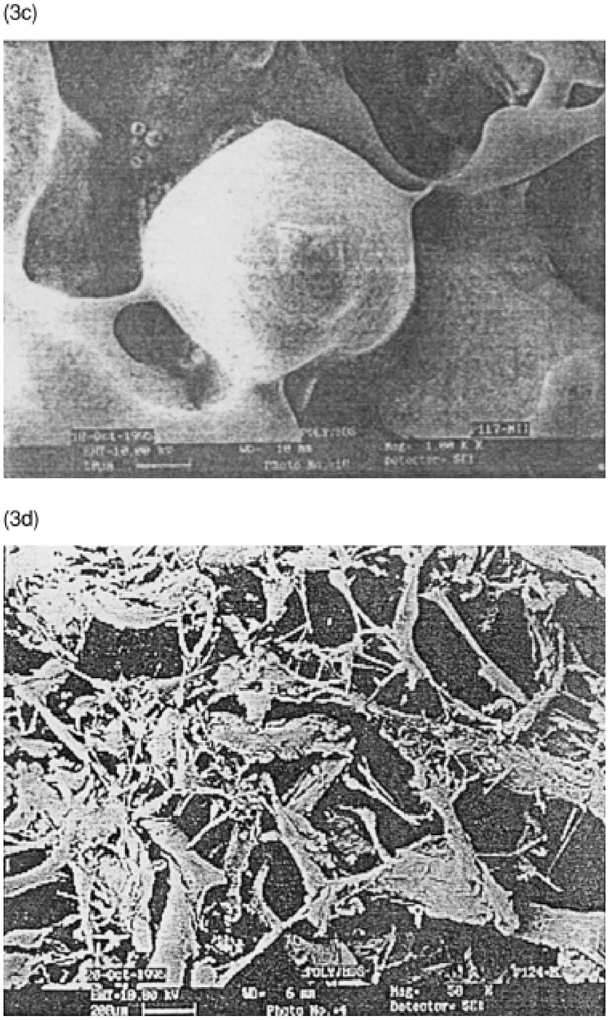

**Figure 6** (3c,d) Samples C and D analyzed after crystallizing by annealing at 160ºC. Big vesicles and fibrillar structure can be seen in 3c and 3d.

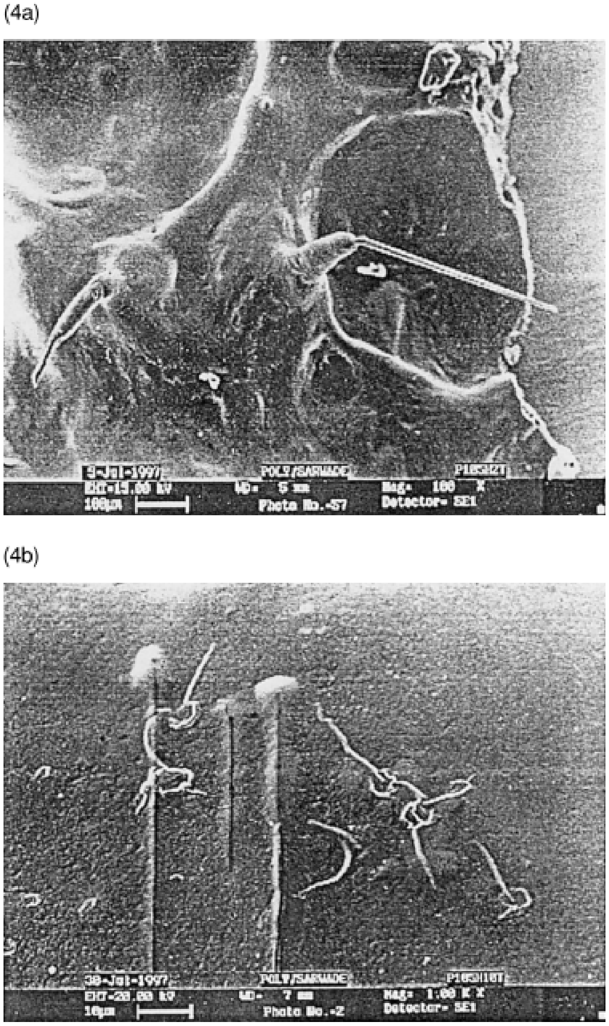

**Figure 7** (4a–d) Morphology of sample A after repetitive heating, that is, 4a shows the morphology after two times of heating and 4b after 10 times. Lamella, chain folding, and developing spherules can be seen.

and the $T'_m$, the more random is the distribution of the residual acetyl groups at equal concentration. The structure of the ACA copolymer consists of pairs of long-chain molecules held together by hydrogen bonds. These double chains all lie along the fiber axis, as determined from X-ray diffraction. The actual position of the hydrogen forming such bonds is not subject to direct experimental methods. Using X-ray, only their effect on the interactomic distances gives evidence of their whereabouts.[26] Schaerer Bayle and Mazee analyzed the thermodynamic data for highly purified *n*-paraffin in the series $C_{21}$–$C_{30}$. They calculated the heats of fusion of the crystalline form stable at low temperature, with their respective melting points included in an appropriate manner and the contribution due to the transition that occurs below the melting temperature. It has been observed that the melting temperature of a polymer is governed, to a large extent, by its entropy of fusion. This behavior is characteristic of polymers because of the increased configurational freedom gained by the chain segments on melting.[31]

There was a decrease in the melting temperature, heat of fusion, and mass of the sample after repetitive heating of the copolymer. Weight loss of about 1 mg and a decrease of 20 J/g heat of fusion was observed after 10–11 times of repetitive heating. The data obtained are given in Table I. All these changes can be attributed to thermal degradation or depolymerization of the copolymer. Thermal degradation of the copolymer can be divided roughly into two general categories: random chain scission and depolymerization. Random chain scission can be visualized as the reaction sequence approximating the reverse of polycondensation; chain scission occurs at random points along with a relatively high molecular weight. The second type of degradation process is essentially a depolymerization process in which monomer units are released from the chain ends; such a process can be viewed as the opposite of the propagation step in

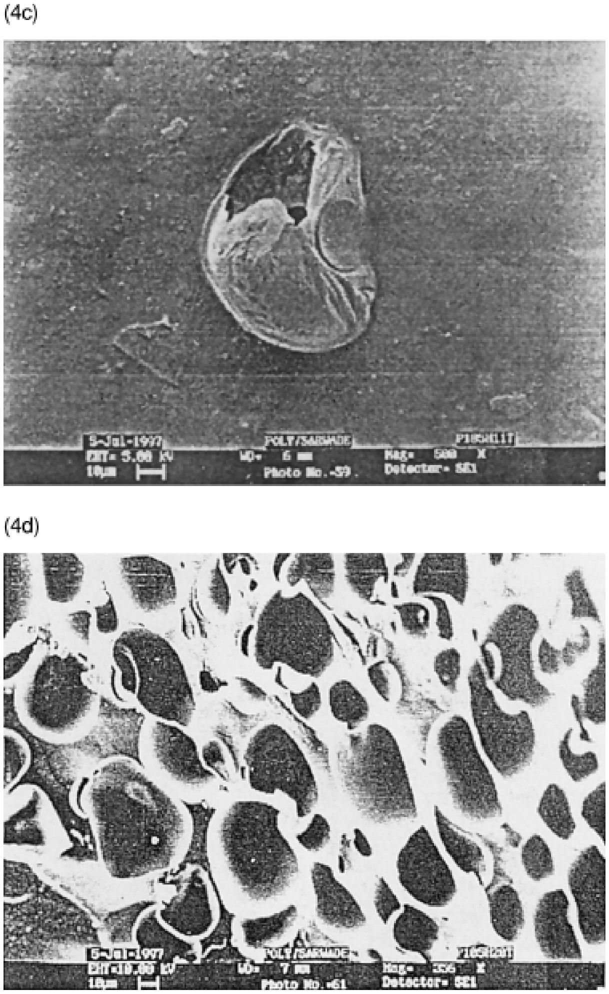

**Figure 8** (4c,d) Morphology of sample A after repetitive heating: 4c after 11 times and 4d after 20 times heating. Lamellae and broken vesicles can been seen.

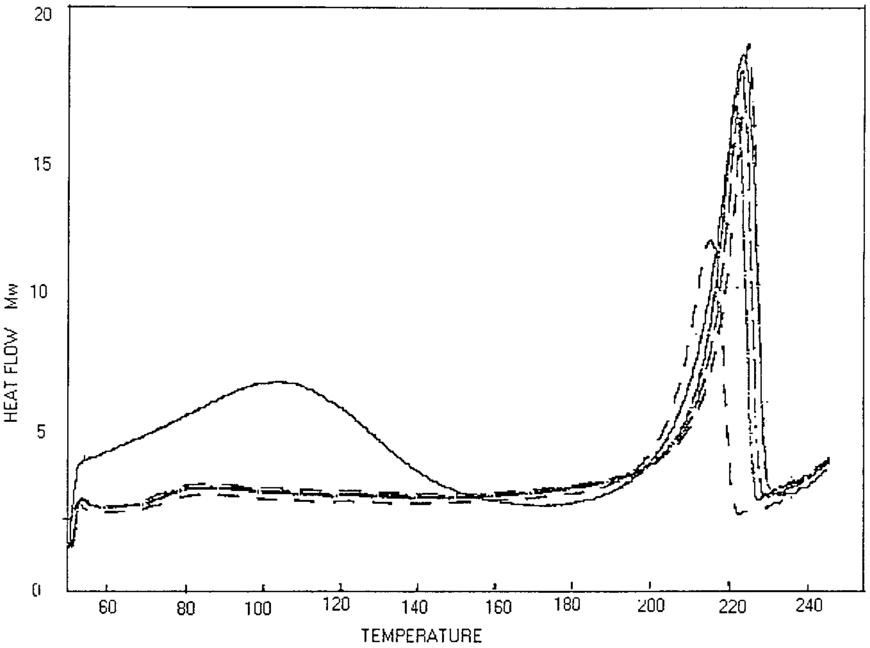

**Figure 9** A decrease in the melting temperature of ACA copolymer with repetitive heating is shown.

addition polymerization. This process is encountered most prevalently with vinyl polymers and polymers produced from cyclic monomers. For a polymer distributed exponentially, it has been shown that, on the assumptions used, the initial distribution survives any amount of end-activated depolymerization. The nature of the chain ends was also assumed to be invariant. The mass decay due to monomer removal must follow the first-order law.[32]

It is possible to distinguish between the production of volatiles by inter- and intramolecular transfer from the nature of the product themselves. If the nonmonomeric fragments are produced by intramolecular transfer near the chain ends, it follows that, since the rates of both monomer and nonmonomer production are proportional only to the concentration of long-chain radicals, the ratio of a monomer to a nonmonomer should be constant throughout the reaction at any fixed temperature.[32]

Futama and Tanaka used mass spectrometry to identify the product of thermal treatment of PVA films; water and acetaldehyde were found as the major volatile products. Generation of the vapor fit the first-order reaction, with the reaction constant *k* of the order of $10^{-4}$ $\text{min}^{-1}$.[33]

## CONCLUSIONS

In the ACA copolymer, after annealing the sample for crystallization, vesicles and lamellar structures were observed in the scanning electron micrographs. The thermal history and presence of microdomains resulted in different morphologies, like spheroids, spherulites, lamellae, and micelles, in the sample heated to the melting temperature and cooled to room temperature without annealing. In the scanning electron micrograph of the sample annealed at 160°C, broken vesicles were seen. Supersaturating along with the change in temperature with evaporation may lead to the formation of continuous coherent gel-like or big vesicles. A decrease in the melting temperature after repetitive heating can be attributed to a first-order depolymerization reaction.

The author thanks Dr. B. D. Sarwade for the SEM analysis and Dr. S. Sivaram, Deputy Director and Head, Polymer Chemistry Division, National Chemical Laboratory, Pune, India, for his encouragement.

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