

Effect of Crystallinity on Surface Morphology and Light Transmittance of Poly(vinylidene fluoride-co-hexafluoropropylene) Thin Film

Sang Goo Lee,¹ Jong Sung Lee,² Jong-Wook Ha,¹ In Jun Park,¹ Soo-Bok Lee,¹ Jong Dae Lee³

¹Division of Green Chemistry, Korea Research Institute of Chemical Technology, Yuseong, Daejeon 305-343, Korea

²Center for Chemical Analysis, Korea Research Institute of Chemical Technology, Yuseong, Daejeon 305-343, Korea

³Department of Chemical Engineering, Chungbuk National University, Cheongju, Chungbuk 361-763, Korea

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ABSTRACT: Homopolymer of vinylidene fluoride and its copolymers containing hexafluoropropylene (HFP) were prepared from free radical solution polymerizations and spin-coated on the glass slides to fabricate thin film with a thickness of $\sim 1 \mu\text{m}$. It was found that the surface morphology of fluorinated thin films was strongly dependent on the crystallinity of polymers. In addition, the surface morphology was the most important factor to determine the optical transmittance of glass coated with the fluoropolymer thin

film. As decreasing the crystallinity of the polymer by introducing HFP with a bulky CF_3 moiety, the surface of thin film became flattened and the transmittance of visible light was increased by reducing scattering. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3331–3337, 2009

Key words: crystallinity; surface morphology; optical transmittance; poly(vinylidene fluoride-co-hexafluoropropylene)

INTRODUCTION

Fluorinated polymers exhibit a number of interesting properties, such as high thermal and chemical stabilities, low water adsorption, excellent weatherability, resistance to oxidation and solvent, low flammability, and low surface free energy.^{1–5} These extraordinary properties arise from mainly fluorine atoms in the polymer chains, which are forming strong covalent bonding with carbon as well as shielding the carbon-carbon backbone from environmental stimuli.

Polyvinylidene fluoride (PVDF) and its copolymer with other fluorinated monomers have been utilized in a variety of industrial fields for many years. Copolymers with hexafluoropropylene (HFP) are one of the most important examples among them. The conventional applications of P(VDF-co-HFP) can be classified into two categories depending on the crystallinity of polymers. Copolymers containing ~ 5 –15 mol % HFP, also known as flexible PVDF, are thermoplastic and semicrystalline. These low HFP content copolymers are used in many applications ranging from tubing, valves and fittings, cable

to membranes. On the other hand, when the HFP content is higher than 20 mol %, the copolymers become amorphous and elastomeric. These elastomers are used mainly as polymer processing aids to improve extrusion, blow molding, and in sealing such as in gaskets and O-rings.

In a recent years, P(VDF-co-HFP) has attracted a great deal of attention as a crucial material in the application of information technology (IT)^{6–11} because of their unique electrical properties, such as ferroelectricity, piezoelectricity, or pyroelectricity.^{12,13} More recently, the rapid growth of researches related with photovoltaic system has broaden the potential application of P(VDF-co-HFP) further. P(VDF-co-HFP) as well as other fluorinated polymers, such as polyvinyl fluoride (PVF) and terpolymer composed of VDF, HFP, and tetrafluoroethylene (TFE), have been investigated as a surface filler in photovoltaic system to cover the concavities and convexities of photovoltaic element and to provide adhesion to surface film,¹⁴ and as polymer electrolytes for dye-sensitized solar cells. It has been shown that P(VDF-co-HFP) can be also utilized in antireflection polymer film coatings as a low refractive index coating composition.¹⁵ It is obvious that the transmittance of light is one of prerequisite properties to these applications as well as weatherability, adhesion, and heat resistance.

However, the studies on the optical properties of thin films of semicrystalline P(VDF-co-HFP) coated

Correspondence to: I. J. Park (ijpark@kRICT.re.kr).

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on the transparent substrates are relatively rare in spite of their importance in industrial applications. In this work, we considered the effect of surface morphology of P(VDF-*co*-HFP) thin film on the transmittance of the glass substrates in the visible wavelength region. To gain a better understanding, semicrystalline PVDF homopolymer and its copolymers with HFP having different degree of crystallinity were synthesized, and the relationship between light transmittance and crystalline character of polymers was investigated.

EXPERIMENTAL

Materials

Vinylidene fluoride ($\text{CH}_2=\text{CF}_2$, VDF, 98%) and hexafluoropropylene ($\text{CF}_3\text{CF}=\text{CF}_2$, HFP, 99%) were purchased from Apollo Scientific (Cheshire, United Kingdom) and 3M (Oakdale, MN), respectively. Diisopropylperoxy dicarbonate ($((\text{CH}_3)_2\text{CHOOCO}-\text{COOCH}(\text{CH}_3)_2$, DIPPDC, 27 wt % in acetone) was obtained from Hosung Chemex (Seoul, Korea). 1,1,2-Trichlorotrifluoroethane ($\text{CFCl}_2\text{CF}_2\text{Cl}$, R-113) and *N,N*-dimethylformamide (DMF) were purchased from Aldrich (St. Louis, MO) and DC Chemical (Seoul, Korea), respectively. All reagents were used without further purification. Glass slides (Matsunami Glass, S-1111, Tokyo, Japan) were used as coating substrates after UVO cleaning (Jelight Company (Irvine, CA), 144AX-220-60) for 20 min.

Synthesis of polymers

Three kinds of polymers containing VDF were prepared from solution polymerization using DIPPDC as a free radical initiator. Typically, 0.19 g of DIPPDC and 50 mL of R-113 were charged into a 300 mL stainless steel autoclave under N_2 atmosphere. The reaction mixture was cooled to -10°C and then predetermined amounts of gaseous VDF or VDF and HFP monomers were added into the reactor as listed in Table I. The temperature of reaction mixture was increased and maintained at 45°C with stirring to initiate polymerization. The polymerization was

stopped intentionally by venting remaining monomers when the total conversion reached to 20%. The conversion of monomers was estimated from total pressure inside the reactor comparing with initial total pressure. After evaporation of R-113 and acetone, the crude polymerization product was purified further by precipitation in methanol three times and finally dried under reduced pressure at 60°C for 24 h.

Characterization of synthesized polymers and thin films

Chemical composition and monomer sequence of synthesized polymers were determined by ^{19}F Fluorine nuclear magnetic resonance spectroscopy (^{19}F -NMR, Bruker DRX-300, Am Silberstreifen, Germany). Sample was dissolved in acetone- d_6 with a concentration of 8 wt %. Molecular weight was determined using a gel permeation chromatography (GPC, high temperature PL 220, Waters, Milford, MA) equipped with a refractive index detector and two PLgel-10 μm Mixed-B columns (Polymer Laboratory, Shopshire, United Kingdom). The analysis was performed at 80°C and DMF was eluted with a flow rate of 1.0 mL/min. Polystyrenes with narrow molecular weight distribution ranging between 2000 and 2,000,000 g/mol were used as standards. The thermal properties were measured by a differential scanning calorimeter (DSC, TA Instruments DSC 2910, New Castle, DE). Samples were heated from -70 to 200°C at a rate of $10^\circ\text{C}/\text{min}$ and then cooled to -70°C with the same rate. The melting temperature (M_w) and glass transition temperature (M_w) were determined from the second heating curves. The crystallinity of PVDF and copolymers with HFP were calculated from eq. (1).

$$\text{Crystallinity} = \Delta H / \Delta H_c \times 100(\%), \quad (1)$$

where $\Delta M_w = 104.5 \text{ J/g}$ is the melting enthalpy of PVDF with 100% crystallinity.¹⁶

Polymers were dissolved in DMF at room temperature for 1 day to obtain homogeneous solutions. The concentrations were ranged from 16 to 20 wt % to adjust the thickness of thin films around 1 μm .

TABLE I
Characteristics of Polymers

Polymer	Amounts of monomer		Feed composition VDF (mol %)	Polymer composition ^a VDF (mol %)	GPC		DSC			Yield (g)
	VDF (g)	HFP (g)			M_w (kg/mol)	PDI	T_m ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)	cryst. (%)	
PVDF	14.08	0	100	100	90.0	1.85	174.9	-45.5	54.2	2.85
HFP11	11.27	6.60	80	88.97	90.3	1.84	112.9	-31.2	16.2	3.20
HFP17	9.86	9.90	70	83.01	86.0	1.57	n.d.	-27.6	n.d.	3.40

^a Determined by ^{19}F -NMR.

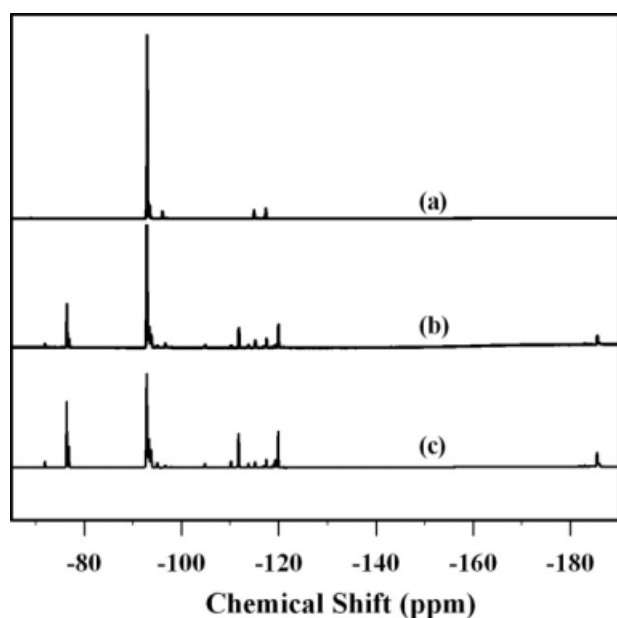


Figure 1 ^{19}F -NMR spectra of synthesized polymers: (a) PVDF, (b) HFP11, and (c) HFP17.

The polymer thin films were coated on a single side by pouring 600 μL of the solution onto the glass slide (25 mm \times 25 mm area and 1.0 mm thickness) and then spin-coated at 1200 rpm for 20 s using a spin coater (photo-resist spinner EC101DT-R790, Headway Research, Garland, TX). The polymer thin films were annealed at 200°C for 12 h and cooled from 200 to 20°C with a cooling rate of 1°C/min to fully develop the crystalline structure. Thickness of polymer films was measured by spectroscopic ellipsometer (Woollam M2000D, Lincoln, NE). Microstructures of polymer films were observed by attenuated total reflection-infrared spectroscopy (ATR-IR, Equinox55, Am Silberstreifen, Germany) in the range of 4000–700 cm^{-1} with a resolution of 8 cm^{-1} . The direct transmittance, which is defined as the fraction of the incident intensity that does not deviate from the incident direction,¹⁷ was measured by a UV-vis spectrophotometer (Jasco V550, Tokyo, Japan) in a range from 350 to 800 nm. In this study, the light was incident in normal direction. The total transmittance of glass substrates coated with polymer thin film was measured by using integrating sphere.

Surface morphology of polymer films was observed by scanning electron microscope (SEM, JEOL JSM-840A, Tokyo, Japan) with an accelerating voltage of 5 or 10 kV. Platinum was sputtered on the polymer films using a cressington 108 auto sputter coater. Three-dimensional surface morphology and surface roughness of polymer films were observed by atomic force microscope (AFM, Seiko Instruments SPA 400, Chiba, Japan) in tapping mode under the atmospheric condition.

RESULTS AND DISCUSSION

Synthesis of polymers

The homopolymer of PVDF and random copolymers of P(VDF-co-HFP) were synthesized by solution radical polymerizations at 45°C using DIPPDC as an initiator in R-113 solvent. The monomer conversion was restricted around 20% to obtain even distribution of monomer segment in polymer chains. Maximum pressure of the polymerization reaction was 7.0–8.3 bar at 45°C depending on monomer composition. Synthesized polymers have a similar molecular weight (86,000–90,300 g/mol) with a relatively narrow molecular weight distribution as shown in Table I. Another important characteristics of polymers used in this study are also listed in Table I.

Chemical composition and monomer sequence

The chemical composition of copolymers was controlled by the monomer feed concentration (20–30 mol % HFP) and determined by ^{19}F -NMR analysis. As shown in Figure 1, ^{19}F -NMR spectrum of P(VDF-co-HFP) exhibits three major regions originated from CF_3 (–68 to –80 ppm), CF_2 (–90 to –130 ppm), and CF group (–180 to –190 ppm), respectively.¹⁸ The monomer composition in copolymers could be calculated from the areas of CF_3 and CF_2 groups in ^{19}F -NMR spectrum.

^{19}F -NMR spectrum provides information not only on monomer composition but also on copolymer chain sequence. In comparison with PVDF [Fig. 1(a)], new peaks can be observed in CF_2 group region because of the attachment of –CF or – CF_3 groups in HFP segments to VDF segments in copolymer chains. The new resonance peaks originated from HFP also appear clearly in the range of –68 to –80 ppm and –180 to –190 ppm, which can be assigned to CF_3 and CF groups, respectively. The detailed assignment of chemical shifts and corresponding sequence analysis are summarized in Table II.

Effect of HFP unit on crystalline property

It is known that the PVDF homopolymer has very strong intermolecular forces that it shows semicrystalline structure of more than 50% crystallinity with different crystal phases as α , β , and γ .^{19,20} Copolymerization of VDF with HFP lowers the crystallinity of resulting polymers because the bulky CF_3 groups contained in HFP hinder the arrangement of copolymer chains.²¹ Figure 2 shows the DSC curves of PVDF and two copolymers HFP11 and HFP17. The most noticeable change can be found is that the melting temperature of HFP11 was dramatically decreased from 174.9°C, the melting temperature of PVDF, and the degree of crystallinity was much

TABLE II
¹⁹F-NMR Chemical Shift of Fluorinated Groups in PVDF and P(VDF-co-HFP)

Chemical shift (ppm)	PVDF	P(VDF-co-HFP)
-71.41		-CH ₂ CF ₂ CF(CF ₃)CF ₂ CH ₂ -
-75.93		-CF ₂ CF ₂ CF(CF ₃)CH ₂ CF ₂ -
-92.35	-CF ₂ CH ₂ CF ₂ CH ₂ CF ₂ -	-CF ₂ CH ₂ CF ₂ CH ₂ CF ₂ -
-93.22		-CF ₂ CH ₂ CF ₂ CH ₂ CF(CF ₃)CF ₂ -
-95.62	-CH ₂ CH ₂ CF ₂ CH ₂ CF ₂ -	-CH ₂ CH ₂ CF ₂ CH ₂ CF ₂ -
-104.35		-CF ₂ CH ₂ CF ₂ CF(CF ₃)CF ₂ -
-109.72		-CF(CF ₃)CH ₂ CF ₂ CF ₂ CF(CF ₃)-
-111.29		-CF ₂ CH ₂ CF ₂ CF ₂ CF(CF ₃)-
-113.30		-CF(CF ₃)CH ₂ CF ₂ CF ₂ CF(CF ₃)-
-114.43	-CF ₂ CH ₂ CF ₂ CF ₂ CH ₂ -	-CF ₂ CH ₂ CF ₂ CF ₂ CH ₂ -
-116.85	-CH ₂ CF ₂ CF ₂ CH ₂ CH ₂ -	-CH ₂ CF ₂ CF ₂ CH ₂ CH ₂ -
-119.44		-CH ₂ CF ₂ CF ₂ CF(CF ₃)CH ₂ -
-182.45		CF ₂ CF ₂ CF(CF ₃)CF ₂ CH ₂
-185.03		-CF ₂ CF ₂ CF(CF ₃)CH ₂ CF ₂ -

lower than PVDF. In addition, in case of HFP17, the melting temperature was hardly observed. The sequence analysis based on ¹⁹F-NMR spectroscopy also indicated that the incorporation of HFP prevents the formation of VDF head-to-tail sequence, and thus, produced polymers with less crystallinity as found in DSC analysis. A number of previous studies have confirmed that copolymers containing about 5–15 mol % HFP are thermoplastic and semicrystalline. In addition, further increase of HFP content shows amorphous and elastomeric characteristics,^{22,23} that is well agreed with the results shown in Figure 2. On the other hand, glass transition temperature of copolymers (Table I) was increased with HFP contents. It might be due to that the bulky CF₃ groups attached to the polymer backbone reduced the flexibility of the polymer chain.

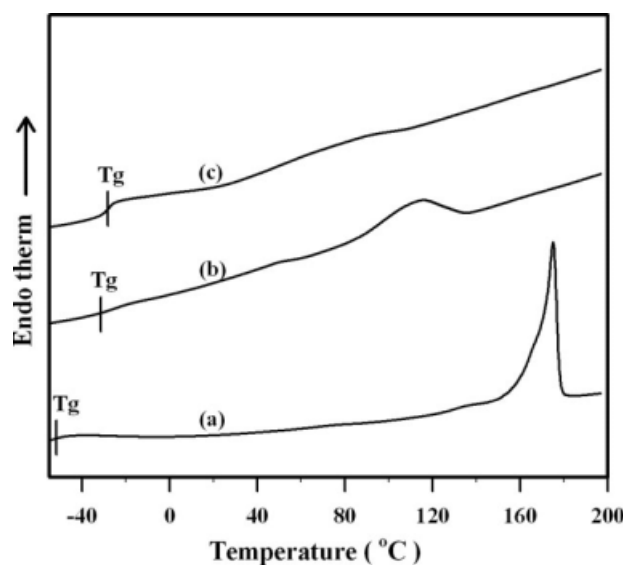


Figure 2 DSC thermograms of synthesized polymers: (a) PVDF, (b) HFP11, and (c) HFP17.

It has to be noted that the crystalline character of thin films can be significantly different because the aforementioned thermal properties were measured from bulk polymer samples. Thus, the crystalline structure and the relative portion of crystalline to amorphous phases of the thin films were investigated qualitatively using ATR-IR analysis. Figure 3 shows ATR-IR spectra of PVDF and copolymers slowly cooled after annealing at 200°C. Absorption band at 1288 cm⁻¹ stands for the ferroelectric crystalline phase (β -phase)¹⁹ and the absorption bands at 1217, 1069, 978, 801, 761 cm⁻¹ are associated with paraelectric crystalline phase (α -phase) of PVDF and P(VDF-co-HFP).²⁴ The intensities of every absorption bands responsible for crystalline phases became weak and broad in copolymer films, which means that part of crystalline phase in polymer film changes amorphous

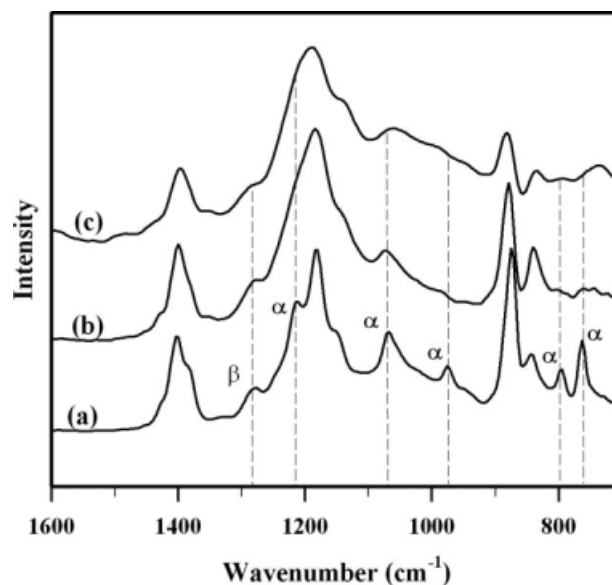


Figure 3 ATR-IR spectra of polymer thin films: (a) PVDF, (b) HFP11, and (c) HFP17.

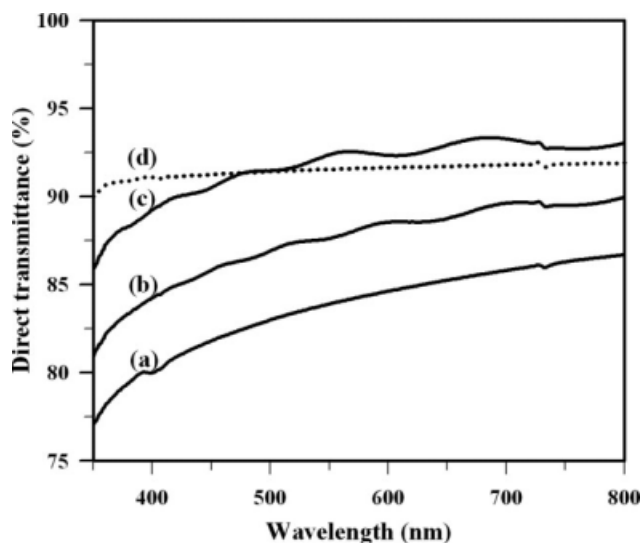


Figure 4 The direct transmittance spectra of spin-coated glass slides: (a) PVDF, (b) HFP11, (c) HFP17, and (d) bare slide glass.

phase with increase of HFP repeating units. These results are coincident with thermal behavior of P(VDF-co-HFP) copolymers at least qualitatively.

Effect of crystallinity on surface morphology and optical transmittance

In a viewpoint of optical properties of thin solid film, especially of visible light transmittance, the refractive index of material is a crucial factor. Much light is reflected at the air-material interface as increasing the refractive index of the coating material. On the other hand, when the transparent substrate is coated with a thin layer of dielectric material, reflections from the outer surface of the film and the outer surface of the substrate can be cancelled each other by destructive interference. As a result, if coating material has the lower refractive index than substrate, the light transmittance increases to some extent compared with the bare substrate.

One of promising effects can be expected by incorporating HFP in the copolymers is the reduced refractive index. The refractive index of fluorinated polymer is generally dependent on the volume fraction of fluorine contained within the polymer. By increasing HFP content, or in other word, increasing fluorine content in the copolymer, the refractive index of copolymers can be lowered. For example, the refractive index of PVDF homopolymer was 1.40 (literature value = 1.42), whereas that of HFP11 was 1.36 at 580 nm according to the analysis carried out by an ellipsometer for 1 μm thickness thin films.

The direct transmittance spectra of glass slides coated by PVDF and P(VDF-co-HFP) copolymers are

shown in Figure 4. Glass substrate with the refractive index of 1.52 shows uniform transmittance around 91.0% within the visible light range (from 400 to 700 nm). The glass slide spin-coated by HFP17 shows slightly enhanced direct transmission compared with bare slide glass, which means that the destructive interference of light occurred because of the presence of low refractive index thin film on the glass slide. However, transmittance of glass slide coated with PVDF decreases largely. The direct transmittance of glass slide coated with HFP 11 is higher than that of PVDF coated one. However, even though destructive interference patterns are observable in transmittance spectrum in this case, the direct transmittance is still lower compared with bare glass slide.

Although some electrostrictive and mechanical properties enhanced,²⁵ the optical transmittance is expected to be deteriorated as increasing crystallinity of polymer films. The reduction in transmission intensity is mainly the result of light scattering at the surface or the bulk of semicrystalline film. Inhomogeneity of the medium resulted from the spatial variations of refractive index in the film is responsible for light scattering. Another important parameter to determine light transmittance is the surface structure. According to Stein and Prud'homme,²⁶ the transparency of semicrystalline polymers is dominated not only by the fine scale refractive index fluctuation as a result of the alternating crystalline and amorphous phase layers inside the spherulites but also by the larger superstructures. In addition, a lot of investigations have shown that the majority of light scattering is resulted from the surface roughness, and in this case, the dominating cause for such roughness is crystallization on and beneath the surface.^{27–31} Therefore, we assume that the transmittance loss of PVDF and HFP11 thin films can be attributed to light scattering from surface textures derived from crystalline domain and its grain boundaries.

Figure 5 illustrates surface morphology of the PVDF and P(VDF-co-HFP) copolymer films. PVDF film displays typical spherulite-packed crystalline microdomains with fibrous shape. The average of spherulite size is 40–50 μm in diameter. By contrast, tightly packed wrinkles without spherulite and its boundary are found in HFP11 film. Further increasing of HFP content in the copolymer makes the film surface considerably uniform. Figure 5 also contains AFM 3D images and surface height profiles of the PVDF and P(VDF-co-HFP) copolymer films. PVDF film shows well-developed fibrous surface textures directing oppositely with the root mean square roughness of 16.3 nm. Semicrystalline HFP11 thin film has rough surface with large crag. Even though the root mean square roughness calculated from the scanned images of PVDF and HFP11 films was

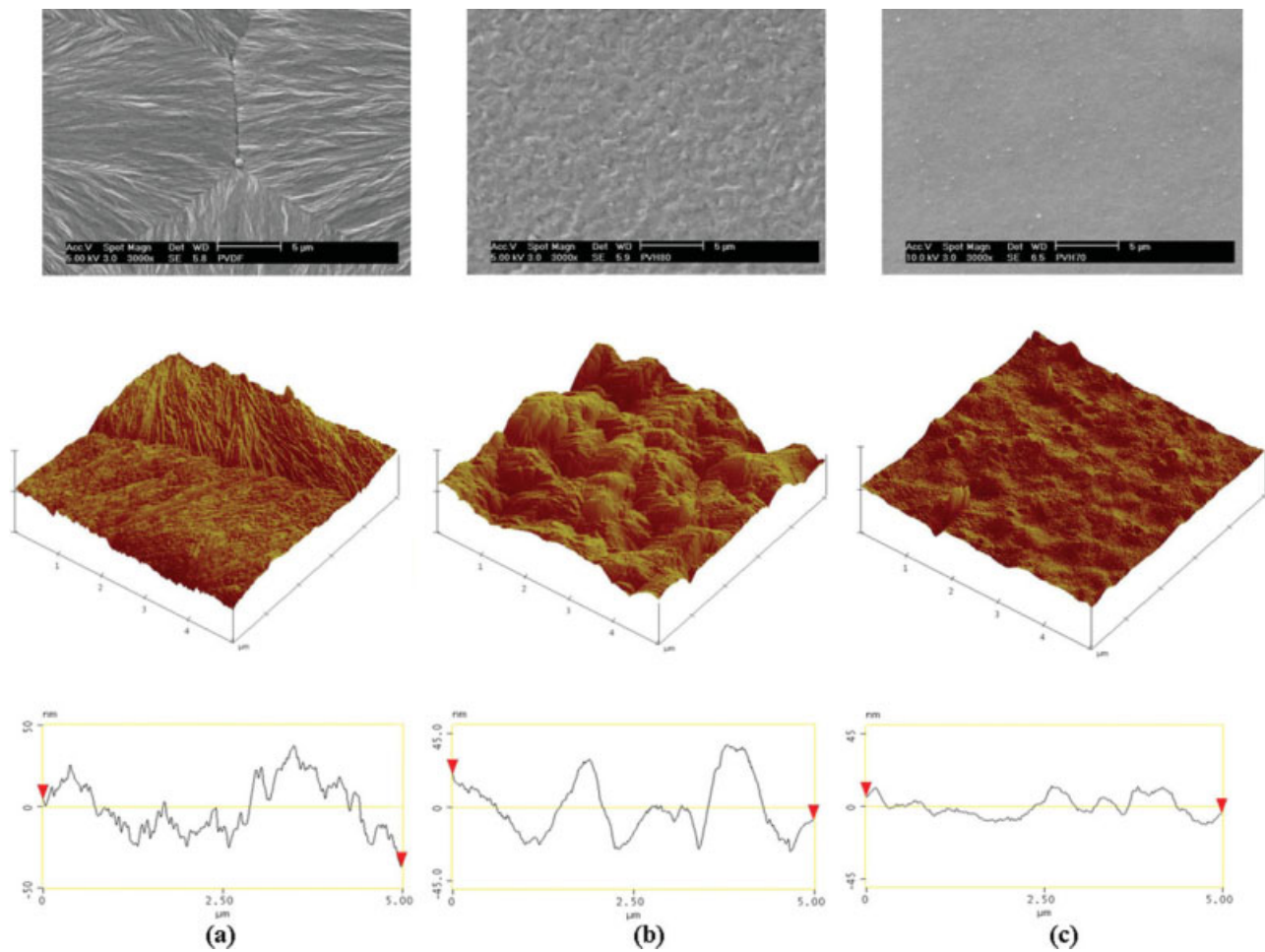


Figure 5 SEM and AFM 3D images (scan area of $5 \times 5 \mu\text{m}^2$) with surface height profile of polymer thin film: (a) PVDF, (b) HFP11, and (c) HFP17. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

similar, it is evident that the PVDF thin film has more submicron scale peaks and valleys as found in surface height profiles. In contrast, the surface of amorphous HFP17 thin film was relatively flat.

In Figure 6, the differences between total transmittance and direct transmittance for each sample are represented. In principle, it stands for the intensity of transmitted light deviated from the incidence direction and it must be closely related to the light scattering. As expected, negligible amount of light is scattered in passing through a flat slide glass. The intensity of scattered light increases as polymer film has more crystalline phase and much larger surface roughness.

The optical transmittance of thin films is influenced greatly by surface morphology if the length scale of surface structures is comparable to the wavelength of incident light.^{32–35} In that case, besides light scattering considered mainly in this study, some portion of the incident light also can be reflected at the surface by diffuse reflection in addition to the specular reflection. As a consequence, the

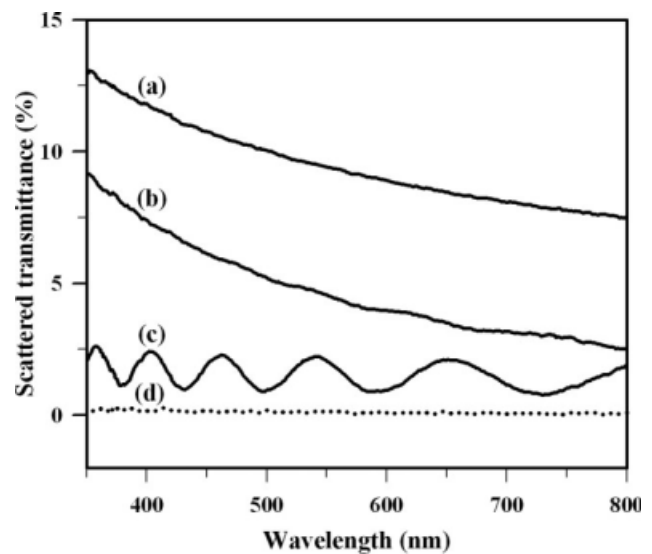


Figure 6 The scattered transmittance spectra of spin-coated glass slides: (a) PVDF, (b) HFP11, (c) HFP17, and (d) bare slide glass.

intensity of transmitted light is reduced much compared with the flat surface composed of the same material. As diffuse reflection is the reflection of light from an uneven or granular surface such that an incident light is seemingly reflected at a number of angles, the effect of the refractive index of the film is also less important.

The surface roughness of thin films observed in this study increases as increasing crystallinity of polymers. Although it is difficult to explain the contributions from the individual effect of spherulites, the interface between amorphous and crystalline phases, and the anisotropy in the spherulites separately, it can be insisted that the surface roughness originated from crystalline microstructures is responsible for the loss of direct transmittance and increment of light scattering.

CONCLUSIONS

Optical transmittance of thin films made from PVDF and P(VDF-co-HFP) copolymers containing 11.03 and 16.99 mol % of HFP has been investigated. Polymers, which featured similar molecular weight and narrow molecular weight distribution, were prepared by solution polymerization with a free radical initiator at low temperature. According to the microstructure analysis on the copolymer chains carried out by ^{19}F -NMR, the portion of VDF head-to-tail sequence was decreased by introducing HFP units in polymer chains. Consequently, the crystallization of polymer chains was prevented considerably by bulky CF_3 groups incorporated within polymer chain as explained from DSC and ATR-IR results. To observe surface morphology with crystalline microdomains and corresponding optical transmittance, spin-coated films on glass slide were crystallized by slow cooling from 200°C . It was found that the crystallinity of the polymers influenced the surface morphology of their thin films. As increasing the HFP content in polymer chains, the surface of thin films became smooth and the direct transmission was increased. It was also found that the direct transmittance of the crystalline thin films was more influenced by surface morphology than intrinsic properties such as refractive index of polymer.

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