

Effect of Isomerization on the Stability of the Surface Aggregation Structure of Chlorinated Polyacrylamide Thin Films on the Basis of Interferometric Observations

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ABSTRACT: Three isomers of chlorinated polyacrylamides were synthesized by a solution polymerization technique. The prepared polymers were dissolved in acetone to prepare 0.1 and 0.05 wt % solution concentrations. Polymer thin films were then prepared by spin-casting from acetone solutions onto a glass substrate. The prepared films were characterized by Fourier transform infrared (FTIR) spectroscopy and annealed at 80°C for 6 h. The surface morphology of the prepared films was studied before and after annealing

with an interference microscope to determine the effect of isomerization on the stability of the polymer thin films. The thin film of the polymer with a chlorine atom in the para-position showed better stability due to the ionic interaction with the glass substrate. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2601–2606, 2002

Key words: polymerization; acetone solutions; thin films; annealing, surfaces; morphology

INTRODUCTION

Polymer thin films are becoming more important from scientific standpoints and technological applications. Numerous studies have addressed the properties of thin polymer films prepared by the spin-casting techniques.^{1–3} Spin-casting represents an economic and straightforward means of creating nanostructure films. Polymeric surface functions, such as in biomaterials, adhesives, lubricants, etc., are closely related to the surface aggregation structure of polymeric solid.^{4,5} In these applications, the films are required to remain homogeneous, stable, and of uniform thickness. Under some circumstances, such as in electronic applications, these film properties are essential even under stringent environmental and thermal treatment.

The dewetting of polymer films from substrates is a phenomenon arising from heating above the glass transition temperature of the polymer. These films break up and spontaneously dewet the substrate, resulting in the formation of droplets.^{6,7} The stabilization of thin polymer films is therefore of an utmost importance for many industrial applications. Usual methods for stabilizing nonwetting films rely on the modification of interfacial tension between polymer and substrate or chemical surface modification of substrate with an end-functionalized polymer.⁸ Also, the entanglement between tethered and free polymer

chains in the thin films can prevent dewetting from occurring, as reported by Yerushalmi et al.⁹ In this study, a trial is made to achieve long-term stabilization of surface aggregation structure for thin films using different isomers of chlorinated polyacrylamides,¹⁰ which are able to form polymer brush adsorbed on the substrate. The effect of isomerization of these polymers on the stability of surface aggregation structure of the polymer thin films prepared from different concentrations is investigated before and after annealing on the basis of interferometric observations.

EXPERIMENTAL

Materials

o-Chloroaniline, *m*-chloroaniline, and *p*-chloroaniline were obtained from Aldrich Chemical Company (UK). Acryloyl chloride was supplied from Merck. *N,N*-azobisisobutyronitrile (AIBN) was obtained from Fluka (Germany). All solvents and reagents used were purified according to standard techniques.¹¹

Polymer synthesis and characterization

Acryloyl chloride was reacted with *o*-, *m*-, and *p*-chloroanilines to afford the corresponding monomers.¹⁰ The three monomers were solution polymerized, using AIBN as a free radical initiator. A constant initiator-to-monomer ratio (1:50) was used for polymerization. A mixture of each of the three monomers (2 g, 11.019 mmol) and AIBN (0.014 g, 0.085 mmol) in 30 mL of tetrahydrofuran (THF) was introduced in a

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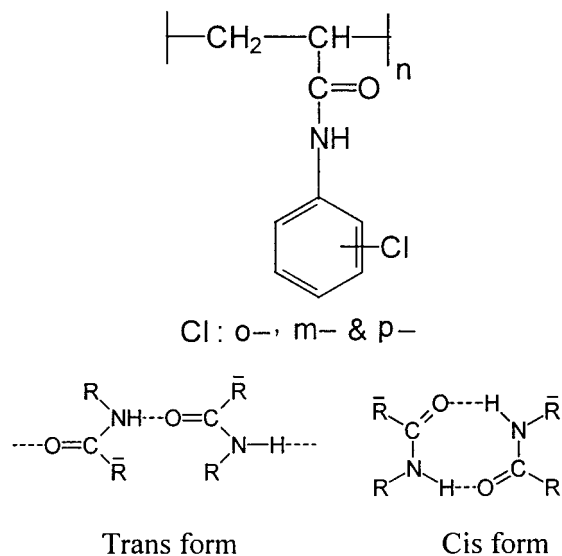


Figure 1 (a): Chemical structure of the prepared polymers. (b): Amide group association between polymer chains in cis and trans conformations.

TABLE I
Physicochemical Properties of the Polymers

Polymer	T_g (°C)	Intrinsic viscosity, dL/g	mp (°C) of monomer
Poly(2-CPA)	63	0.042	96
Poly(3-CPA)	70	0.055	100
Poly(4-CPA)	76	0.220	183

round-bottomed flask under nitrogen flow, and the reaction mixture was kept at 55°C for 14 h. The solvent was vacuum evaporated, and the polymer was dissolved in acetone and then precipitated into hexane. The precipitate was vacuum dried to give the chlorinated polyacrylamides as white powders. Characterization of the prepared monomers and polymers has been published elsewhere.¹⁰ The chemical structure of the three polymers used is shown in Figure 1a.

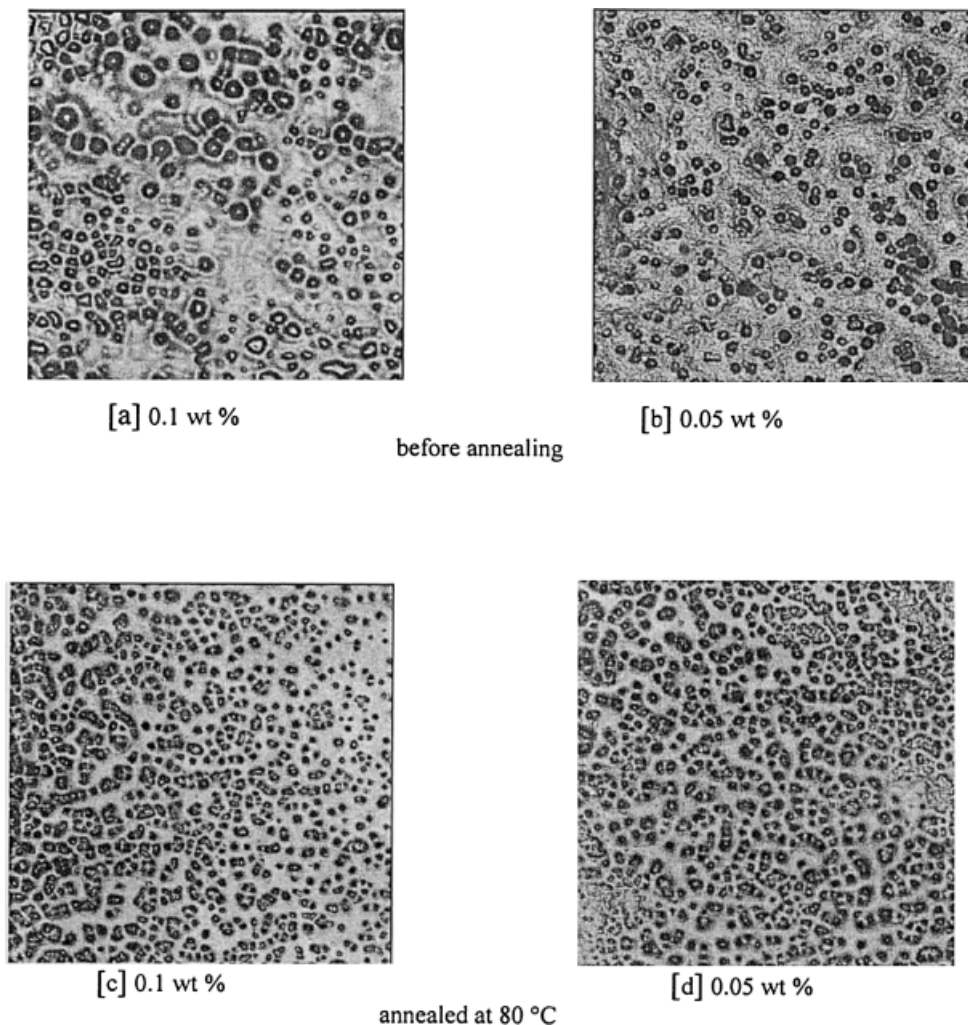


Figure 2 [a–d]: Interference images of poly (2-CPA) thin films prepared from 0.1 wt% and 0.05 wt% polymer solutions before and after annealing.

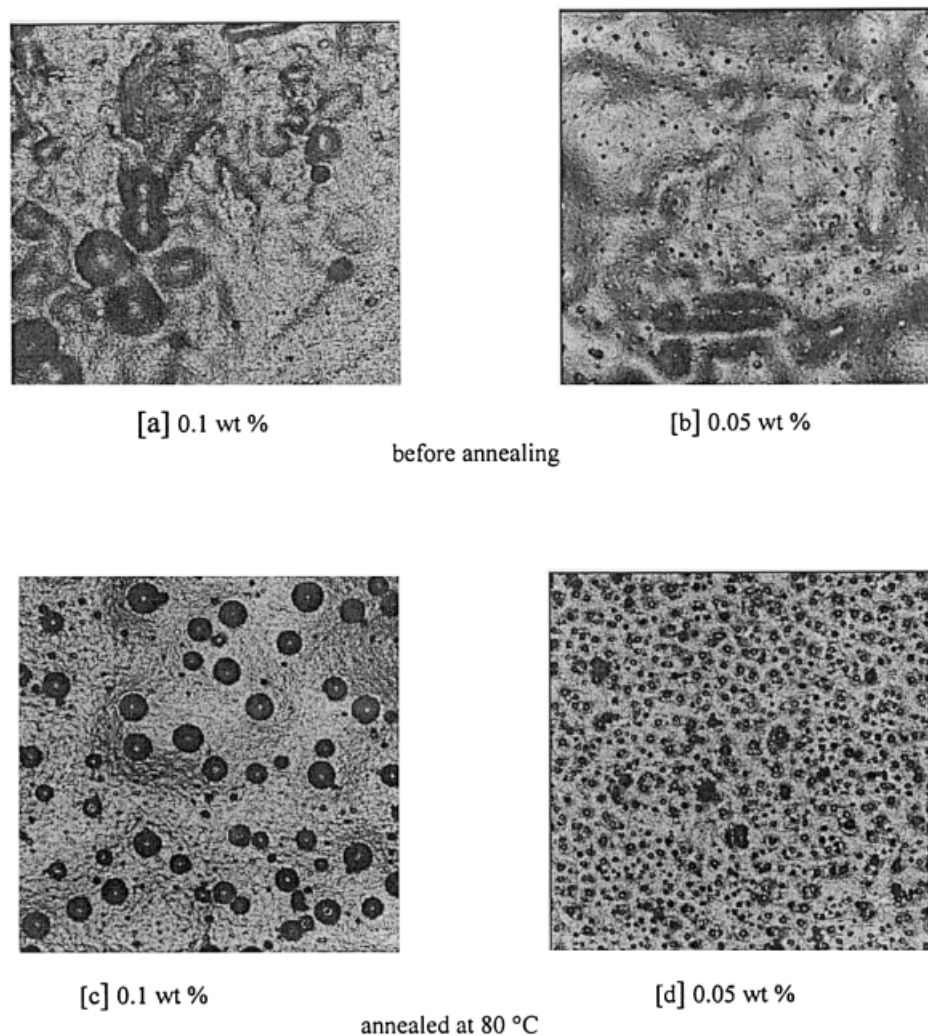


Figure 3 [a–d]: Interference images of poly (3-CPA) thin films prepared from 0.1 wt% and 0.05 wt% polymer solutions before and after annealing.

Bulk glass transition temperatures, T_g of the three polymers used were determined by differential scanning calorimetry (DSC, Shimadzu, DSC-50) at $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Viscosities of the synthesized polymers were measured in dimethyl formamide (DMF) at 25°C at different concentrations (0.2, 0.4, 0.6, 0.8%) with a Core Plate Brook Field Rheometer DV III.¹⁰ Polymer thin films were prepared by spin-casting from acetone solutions of 0.1 and 0.05 wt % onto a glass substrate. Fourier transform infrared spectroscopy (FTIR) analysis was obtained with a Bruker 1600 Spectrometer. The specimens measured were thin films that were spin-coated onto a glass substrate from a 0.1 wt % polymer solution in acetone and annealed at 80°C for 6 h. The thin film thicknesses were estimated from the line profile of each polymer at each polymer solution concentration. The surface morphology of poly(2-CPA), poly(3-CPA), and poly(4-CPA) thin films was investigated with an interference

microscopic (Zygo Maxim -GP 200 Profilometer with $50\times$ Mirau), which produces $1000\times$ magnification.

RESULTS AND DISCUSSION

Bulk characterization

The physicochemical properties of the prepared polymers are summarized in Table I.

The DSC measurements of T_g were in the order poly(2-CPA) < poly(3-CPA) < poly(4-CPA), even though these polymers have almost comparable viscosities. This order indicates that the T_g of poly(4-CPA) is higher than those of poly(2-CPA) and poly(3-CPA). This difference is because of the increase in the apparent molecular weight resulting from the association of the amide groups in the cis confirmation (shown in Figure 1b), which is formed to a greater extent in the case of poly(4-CPA) than in the cases of poly(2-CPA) and poly(3-CPA).

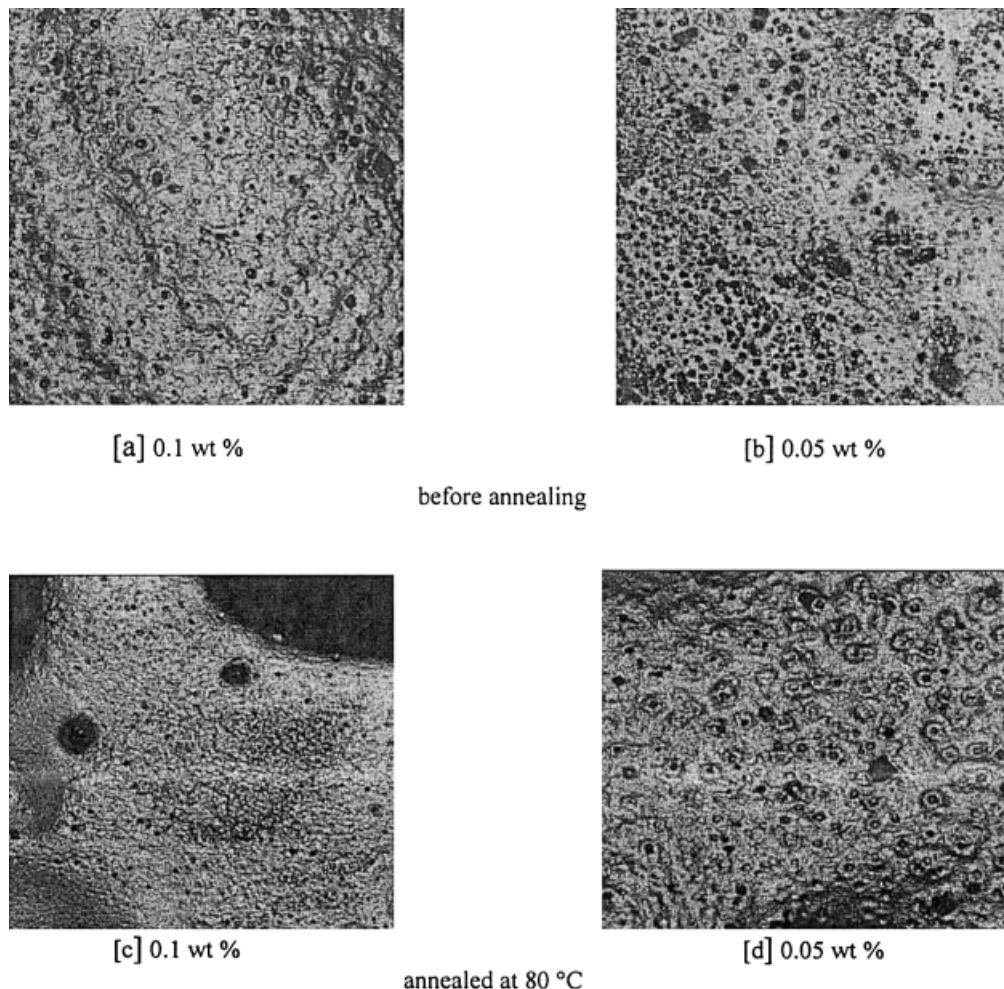


Figure 4 [a–d]: Interference images of poly (4-CPA) thin films prepared from 0.1 wt% and 0.05 wt% of polymer solutions before and after annealing.

Effect of polymer solution concentration on the dewetting of chlorinated polyacrylamides thin films

The chlorinated polyacrylamide thin films were spin-casted onto a glass substrate. The film thickness decreased with the decrease in polymer solution concentration. The interference images of poly(2-CPA) prepared from 0.1 wt % acetone and 0.05 wt %, polymer solutions onto glass substrate are shown in Figure 2. The images were obtained before and after annealing at 80°C for 6 h. The bright part corresponds to poly(2-

CPA) phase, and the darker part corresponds to the bare glass substrate.

The images reveal that poly(2-CPA) dewetted on the substrate with droplet-like structure before and after annealing. It can be noted that the dewetting behavior became more apparent with the decrease in the solution concentration and with annealing treatment above bulk T_g . The dewetting of poly(2-CPA) from glass before and after annealing might be attributed to the absence of a strong interaction between the polymer end groups and the substrate. Also, it can be observed that the roughness of the substrate increased with the decrease in polymer solution concentration and annealing treatment because of the more dewetted structure that was observed.

The images of poly(3-CPA) on a glass substrate from 0.1 and 0.05 wt % acetone solutions, obtained before and after annealing at 80°C for 6 h, are shown in Figure 3. The thin films prepared from 0.1 and 0.05 wt % solutions showed homogenous and continuous structure, being independent of the polymer solution concentrations before annealing, as shown in Figures

TABLE II
Relation between Thin Film Thickness and Polymer Solution Concentration

Polymer	Thickness (nm) at 0.1 wt %	Thickness (nm) at 0.05 wt %
Poly(2-CPA)	7	4
Poly(3-CPA)	8	6
Poly(4-CPA)	10	8

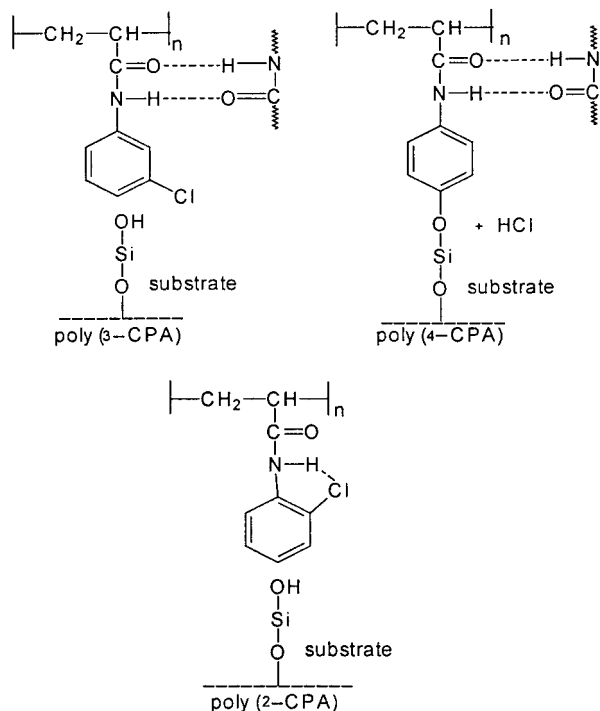


Figure 5 The possible states of interaction between thin films of the prepared polymers and the glass substrate.

3a and b. This result may be due to an entanglement interaction between poly(3-CPA) chain ends that is favored and may cause an increase in its molecular weight and subsequently its T_g in comparison with that of poly(2-CPA). In contrast, the same polymer thin films dewetted from glass substrate after annealing with a hole-like structure, as shown in Figures 3c and d. This result may be explained on the basis that the entanglement association among chain ends is not enough to avoid the dewetting of poly(3-CPA) after annealing. Also, it can be noted from Figure 3c and d that the dewetting of poly(3-CPA) is more evident with annealing and the decrease of polymer solution concentration. However, as the holes of the polymer thin films grow to sufficient size to impinge on each other, we would see a more remarkable change in the dewetting dynamics of poly(3-CPA) than that seen in case of poly(2-CPA). The less extensive dewetting behavior of poly(3-CPA) from the glass substrate in comparison with that of poly(2-CPA) can be attributed to the entanglement association among polymer chain ends.

To enhance the interaction between polymer chain ends and the substrate, poly(4-CPA) was used. The interference images of poly(4-CPA) thin films coated onto glass substrate from 0.1 and 0.05 wt % polymer solutions in acetone before and after annealing at 80°C for 6 h are shown in Figure 4. In the case of poly(4-CPA), a homogenous thin film formed on the substrate before annealing that was independent of the concentration of the polymer solution and annealing treatment, as shown in Figures 4a and b. The film

thickness of poly(4-CPA) prepared from 0.1 and 0.05 wt % solutions was higher than those films of poly(2-CPA) and poly(3-CPA). Because an anchoring of chain end groups to the substrate would influence the polymer chain mobility, annealing had an effect on the molecular aggregation state, as shown in Figures 4c and d. This result can be attributed to the ionic interaction that may occur between the chlorine end groups of poly(4-CPA) and the hydroxyl groups on the glass substrate, in addition to the hydrogen bonding association that may take place among—CONH—groups.

The film thickness variations after annealing with acetone polymer solution concentrations (0.1 and 0.05 wt %) of poly(2-CPA), poly(3-CPA), and poly(4-CPA) thin films are shown in Table II. The film thickness is in the order poly(4-CPA) > poly(3-CPA) > poly(2-CPA). The increase in the thickness of poly(4-CPA) in comparison with those of films of poly(2-CPA) and poly(3-CPA) may be interpreted in terms of the high density of hydrogen bonding association between—CONH—groups and the ionic interaction between chlorine end groups of poly(4-CPA) and—OH groups of the glass substrate.

A schematic representation of the possible states of interaction between chain end groups of the polymers and—OH groups of the glass substrate is shown in Figure 5. It is thought that the—Cl end groups of poly(4-CPA) form links with the—OH groups present on the substrate more readily than hydrogen bonding which is easily dissociated on annealing treatment and results in dewetting of the films from the substrate, as happened in the cases of poly(2-CPA) and poly(3-CPA). These results were confirmed by an FTIR study that indicated the disappearance of the C—Cl bending peak of poly(4-CPA) at 586–594 cm^{-1} as a result of involvement in the ionic interaction with the glass substrate. On the other hand, the C—Cl bending peaks that occur at 586–594 cm^{-1} in the cases of poly(2-CPA) and poly(3-CPA) were observed because the—Cl is not involved in an ionic interaction.

CONCLUSIONS

Poly(4-CPA) thin films prepared from 0.1 and 0.05 wt % showed homogenous structure before and after annealing due to ionic interaction between the chlorine end groups of the polymer and the hydroxyl groups on the glass substrate on one hand and the hydrogen bonding association taking place among the amide groups on the other hand. Poly(2-CPA) and poly(3-CPA) showed dewetted structures after annealing due to the absence of interaction between polymer chain end groups and the substrate. The thin film thickness of poly(4-CPA) was higher than those of poly(2-CPA) and poly(4-CPA). On the basis of these results, poly(4-CPA) is recom-

mended to be used for technological applications like optical materials and permselective membranes.

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