

Surface Free-Energy Analysis of Poly(*N*-vinyl-2-pyrrolidone–crotonic acid) Copolymers Prepared by γ -Ray-Induced Polymerization Technique

Tuncer Çaykara,¹ Zekeriya Yerlikaya,² Ömer Kantoğlu³

¹Gazi University, Faculty of Arts and Science, Department of Chemistry, 06500 Besevler, Ankara, Turkey

²Gazi University, Kastamonu Faculty of Education, Department of Science Education, 37200 Kastamonu, Turkey

³Ankara Nuclear Agriculture and Animal Research Center, Turkish Atomic Energy Authority, Ist. Yolu 30 km Kazan, 06983 Ankara, Turkey

Received 26 September 2002; accepted 30 June 2003

ABSTRACT: Pure poly(*N*-vinyl-2-pyrrolidone) (PVP) and P(VP–crotonic acid) [P(VP/CrA)] copolymers with different CrA contents were prepared by the γ -ray-induced polymerization technique. The change in the surface free energy of the copolymers was investigated using the Van Oss–Good contact angle evaluation methodology in order to estimate their wettability properties. The apolar Lifshitz–van der Waals component (γ_s^{LW}) and the electron donor component (γ_s^-) of the PVP network were calculated as 27.6 and 56.5 mN m⁻¹, respectively. In this case, the surface of the PVP network had a basic character (electron donor). By contrast,

the γ_s^{LW} component of P(VP/CrA) copolymers increased and then remained almost constant with increasing CrA content. In addition, the surface of these copolymers changed from a basic character ($\gamma_s^- = 56.5$ mN m⁻¹) to an acidic character ($\gamma_s^+ = 0.07$ mN m⁻¹) with increasing CrA contents in the copolymer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1893–1897, 2004

Key words: surfaces; radiation; poly(*N*-vinyl-2-pyrrolidone–crotonic acid); networks

INTRODUCTION

N-Vinyl-2-pyrrolidone (VP) is known to be a hydrophilic, adhesion-promoting monomer. Because of its hydrophilic characteristics, polymerization of VP produces hydrophilic materials, which generally possess excellent biocompatibility with living tissues and extremely low cytotoxicity.¹ Poly(VP) (PVP) has been considered as a plasma substitute, a soluble drug carrier, a modifier for enzymes, and a comonomer in UV curable bioadhesives.^{2,3} PVP is also a very good choice for making hydrogels. For example, it is probably the most effective comonomer that is used to increase the water take-up ability of 2-hydroxyethyl methacrylate hydrogels.^{4–6} It has been pointed out that polymers or copolymers containing carboxylic acid groups are highly desirable because such groups represent functionality that is useful for yielding a wide variety of products. Copolymers have the newly available carboxylic acid functional groups, which can be used in any further incorporation of drugs or other bioactive agents.^{7–10}

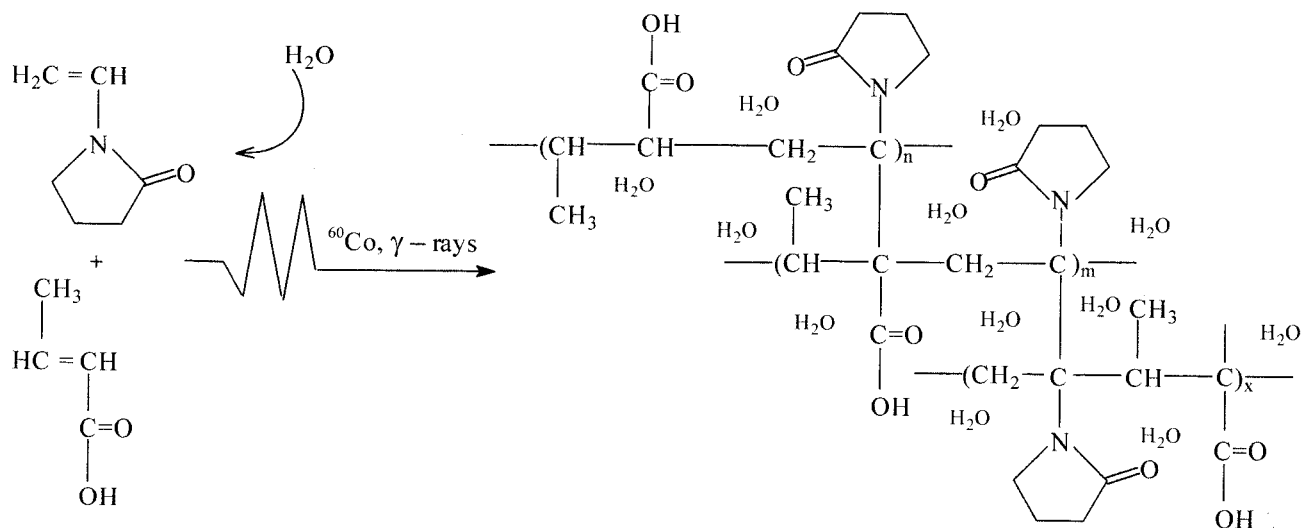
Highly crosslinked PVP polymers are generally prepared from the monomer, with or without some comonomers, in the presence of a crosslinking agent.¹¹ However, γ -ray-induced simultaneous polymerization and crosslinking has some advantages over the other techniques. This technique is generally termed a clean technique, which does not require any extra chemicals and leaves some unwanted residues. It can be applied at any temperature and dose rate.

The surface properties of solid polymers and copolymers are important in many application fields, such as adhesion, coating, printing, and biocompatibility. Contact angle measurements have been made for determining the wettability of various materials. This angle is characteristic of the substances in the systems because of the surface tension of the liquid and the surface energy of the solid. A low contact angle indicates good wettability. As the contact angle increases, the wettability decreases.

Recently, Van Oss and coworkers introduced a theory and practical methodology to estimate the interfacial tensions between apolar and electron donor–acceptor molecules.^{12–15} They assume that the surface and interfacial free energies consist of two components: an apolar or Lifshitz–van der Waals (LW) component and a polar component caused by acid–base (AB) interaction. This methodology was successfully applied to the determination of the surface free energy of polymers.^{16,17}

Correspondence to: Dr. T. Çaykara (tcaykara@hotmail.com).

Contract grant sponsor: Gazi University Research Fund; Contract grant number: 05/2003-50.



Scheme 1 The preparation of P(VP/CrA) hydrogels by a radiation-induced simultaneous process of polymerization and self-bridging of VP and CrA in aqueous solutions without the use of a crosslinker.

In this present work, poly(VP–crotonic acid) P(VP/CrA) copolymers were prepared by the well-known ^{60}Co γ -ray-induced polymerization technique at varying compositions. Contact angle measurements and the evaluation of the surface free energy components by the Van Oss–Good methodology were carried out to analyze the surface free energy properties of these copolymers.

EXPERIMENTAL

Materials

The two monomers used in this study (VP and CrA) were supplied by Merck. The test liquids used in the contact angle measurements were purchased from Merck and BDH and used without further purification.

Preparation of hydrogels

The P(VP/CrA) hydrogels were prepared by a radiation-induced simultaneous process of polymerization and self-bridging of VP and CrA in aqueous solutions without the use of any crosslinker (see Scheme 1). Aqueous solutions of monomers were prepared in 1 mL of pure water in different compositions (VP/CrA mole ratios of 95.4/4.6, 93.1/6.9, 89.9/10.1, and 87.0/13.0). These monomer solutions were placed in glass substrates and irradiated at 16 kGy in air at ambient temperature in a PX- γ -30 Isslodovateji irradiator at a fixed dose rate of 3.36 kGy h^{-1} . The resulting copolymers were separated from the glass substrates. They were then immersed in an excess amount of acetone and gradually placed into distilled–deionized water to remove unreacted monomers.

Contact angle measurements

Rectangular bar films ($1.5 \times 2 \times 15$ mm) were prepared and dried under a vacuum at 333 K for 48 h for the determination of the contact angles of the PVP and P(VP/CrA) copolymers. The specimens were tested for wetting force by placing them in a tensiometer (White Elec. Inst. Co. Ltd.) according to the Wilhelmy plate technique.¹⁸ The wetting force of the meniscus at the long edge of the sample is determined (Fig. 1). The cup including the test liquid is elevated slowly until the short edge of the sample contacts the liquid. The resulting capillary force is measured from which the contact angle (θ) is calculated by the following equation¹⁹:

$$\cos \theta = \frac{F}{p\gamma} \quad (1)$$

where F is the wetting force (mN), p is the perimeter (m), and γ is the surface tension (mN m^{-1}).

Diiodomethane was used as the probe liquid for determining the LW interaction, and ethylene glycol and formamide were used as the probe liquids for determining the AB interactions. Before each experiment with a probe liquid, the specimen was dried in an oven for 0.5 h. Finally, the perimeter of the rectangular bar specimens were determined by using n -decane, which was assumed to make a zero contact angle with the specimen. Table I shows the total surface tension, Lewis AB, and LW components of the test liquids.²⁶ The $\cos \theta$ values were employed in previously described equations to obtain the free energies of the copolymers. To compare the results, the same procedure was applied to a low density polyethylene specimen and its surface free energy was found

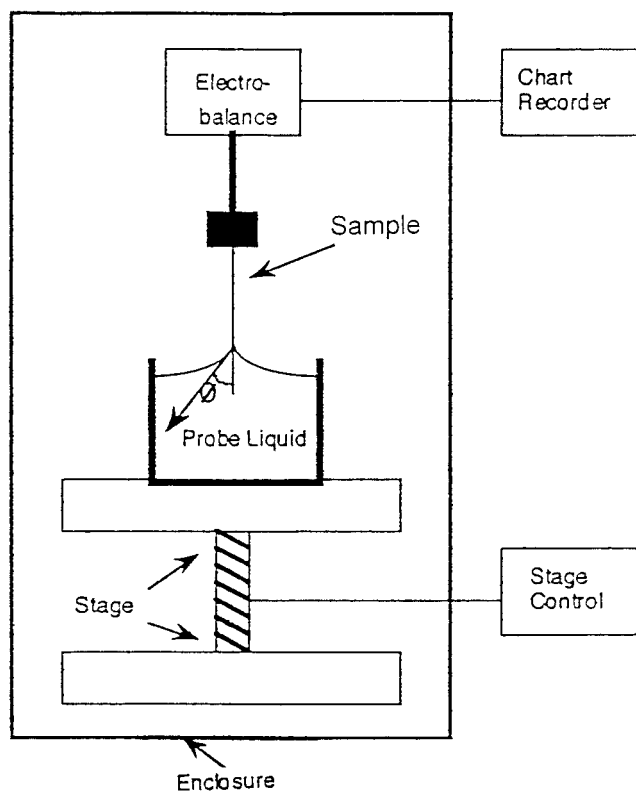


Figure 1 The contact angle apparatus setup.

to be 32 mN m^{-1} , which was in accordance with cited values.²⁰ All measured contact angles were an average of three measurements.

Theoretical background of surface free energy

According to the Van Oss–Good theory,^{12–15} the surface and interfacial free energies (or tensions, γ) of a given nonmetallic material (*i*) consist of two components: an apolar (LW) component of electrodynamic origin (γ_i^{LW}) and a polar component (AB) caused by Lewis interactions (γ_i^{AB}). The two components are additive, yielding a total γ_i^{TOT} :

$$\gamma_i^{TOT} = \gamma_i^{LW} + \gamma_i^{AB} \quad (2)$$

In the following, γ_i^+ and γ_i^- are the respective independent Lewis acid and Lewis base components of the surface free energy:

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-} \quad (3)$$

A characteristic feature of the Lewis acid and base components is their nonadditivity. Hence, if phase *i* possesses only γ_i^+ or γ_i^- , this component does not participate in the total surface free energy of phase *i*. However, it will interact with the complementary component of phase *j*.

The adhesion between a solid (S) and liquid (L) is given as

$$(1 + \cos \theta) \gamma_L^{TOT} = 2\sqrt{\gamma_L^{LW} \gamma_S^{LW}} + \gamma_{SL}^{AB} \quad (4)$$

$$\gamma_{SL}^{AB} = 2[\sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_L^+ \gamma_S^-}] \quad (5)$$

where γ_S^{LW} is the LW component of a solid surface, γ_L^{LW} is the LW component of a liquid surface, γ_{SL}^{AB} represents the short-range Lewis AB interactions, $(\gamma_L^{LW} \gamma_S^{LW})^{1/2}$ represents the LW component, and θ denotes the contact angle of the liquid on the solid surface.

The γ_{SL}^{AB} , γ_S^+ , and γ_S^- values can be determined by using the contact angle subtended by a liquid on a solid surface and the complete Young equation²¹:

$$(1 + \cos \theta) \gamma_L^{TOT} = 2[\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_L^- \gamma_S^+} + \sqrt{\gamma_S^- \gamma_L^+}] \quad (6)$$

The γ_S^{LW} can be found from the contact angle of an apolar liquid. For an apolar liquid, $\gamma_L^+ = \gamma_L^- = 0$ and thus $\gamma_L^{TOT} = \gamma_L^{LW}$. Then, eq. (6) can be written in the form

$$(1 + \cos \theta) \gamma_L^{TOT} = 2[\sqrt{\gamma_S^{LW} \gamma_L^{LW}}] \quad (7)$$

Consequently, the γ_S^{LW} value can be calculated by applying the contact angle of an apolar liquid on the surface of this solid by using eq. (7). When two polar liquids are used, two equations of the form of eq. (6) constitute a set of two simultaneous equations that can be solved for the two unknown properties of the solid γ_S^+ and γ_S^- .

RESULTS AND DISCUSSION

The PVP and P(VP/CrA) copolymers were tested with polar and apolar liquids, and the surface energies and AB properties of these surfaces were determined. Contact angles are the characteristic constants of liquid/solid systems and provide valuable information on the surface energies of solids.^{22–24} The contact angle measurement technique used in this study demonstrated the advantages in the evaluation of wettability, partic-

TABLE I
Total Surface Tension (γ^{TOT}), Lifshitz–van der Waals Surface Tension (γ^{LW}), Lewis Acid–Base (γ^{AB}), Lewis Acid (γ^+), and Lewis Base (γ^-) Components of Probe Liquids (mN m^{-1})

Probe liquid	γ^{TOT}	γ^{LW}	γ^{AB}	γ^+	γ^-
Diiodomethane (apolar)	50.8	50.8	—	—	—
Ethylene glycol (polar)	48.0	29.0	19.0	1.92	47.0
Formamide (polar)	58.0	39.0	19.0	2.28	39.6
<i>n</i> -Decane (apolar)	23.8	23.8	—	—	—

TABLE II
Contact Angle Results of PVP and P(VP/CrA) Copolymers

Samples	Diiodomethane	Ethylene glycol	Formamide
PVP	61.7 ± 0.2	59.0 ± 0.1	53.5 ± 0.1
P(VP/CrA)-1	55.5 ± 0.1	58.8 ± 0.3	56.3 ± 0.1
P(VP/CrA)-2	30.1 ± 0.1	58.5 ± 0.2	58.8 ± 0.0
P(VP/CrA)-3	30.4 ± 0.0	58.4 ± 0.1	68.5 ± 0.2
P(VP/CrA)-4	36.7 ± 0.2	56.6 ± 0.1	70.3 ± 0.1

ularly its ease of use and minimal susceptibility to measurement errors.²⁵

We do not have a wide choice of probe liquids that would give suitable contact angle variations with surface modifications. This is because probe liquids, such as dimethylsulfoxide (DMSO), water, and glycerol, are hydroscopic (i.e., DMSO and glycerol) and may lack high purity (i.e., water) for these types of applications. By contrast, there are numerous studies^{19,21,22,25–27} that indicate suitable applications employing a diiodomethane, ethylene glycol, and formamide triplet as a probe liquid.

The contact angle values of diiodomethane, ethylene glycol, and formamide liquids for PVP and P(VP/CrA) copolymers were calculated by using eq. (1) and are given in Table II. These data were evaluated to determine the surface free energy component of these polymers by the using Van Oss–Good methodology through eqs. (6) and (7). The surface free energy component values of the liquids we used were taken from Van Oss et al.²⁶

The LW surface energy component of the solid material shows the contribution of apolar interactions on the surface energy of the solid. This component forms the greater part of the total surface energy of a material.²² By using eq. (7) and the data obtained from the contact angle measurements for apolar liquids, the γ_S^{LW} values of the PVP and P(VP/CrA) copolymers were calculated and are listed in Table III. The γ_S^{LW} values of the PVP and P(VP/CrA) copolymers were found to be 27.6 and 31.1–44.2 mN m⁻¹, respectively. From the results it is clear that the γ_S^{LW} values of the P(VP/CrA) copolymers at each composition are higher than that of the PVP homopolymer. The remaining electron donor and acceptor components of

TABLE III
Surface Free Energy Components of PVP and P(VP/CrA) Copolymers (mN m⁻¹)

Sample	γ^{TOT}	γ^{LW}	γ^{AB}	γ^+	γ^-
PVP	49.36	27.6	21.76	—	56.5
P(VP/CrA)-1	47.98	31.1	16.88	—	34.0
P(VP/CrA)-2	47.74	44.2	3.54	—	1.5
P(VP/CrA)-3	45.32	44.0	1.32	0.01	—
P(VP/CrA)-4	44.68	41.2	3.48	0.07	—

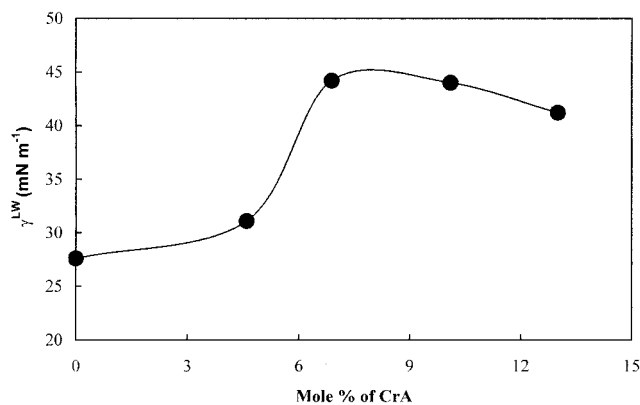


Figure 2 The variation of the apolar Lifshitz–van der Waals component a solid surface free energy (γ_S^{LW}) with the amount of CrA (mol %) in the copolymer.

the surface free energy of the PVP and P(VP/CrA) copolymers (γ_S^- and γ_S^+) were calculated by simultaneously solving the two different forms of eq. (6) that were obtained for the different polar liquids whose γ_L^{LW} , γ_L^- , and γ_L^+ values are known. The surface of the PVP homopolymer was found to have a basic character ($\gamma_S^- = 31.2$ mN m⁻¹). The basic character of the PVP homopolymer was completely neutralized when the percentage of CrA reached 10.1 mol % [P(VP/CrA)-3] in the copolymer. Above this concentration limit of the CrA, the copolymer surfaces became slightly acidic. The γ_S^- and γ_S^+ values in Table III also show that the P(VP/CrA)-1 and P(VP/CrA)-2 copolymers have a basic character whereas the P(VP/CrA)-4 copolymer has a slightly acidic character. As the result, both the acidic and basic character of the surface of these copolymers are greatly dependent on the CrA content in the copolymer.

The changes of the apolar LW component of the surface free energy (γ_S^{LW}) with the CrA content of P(VP/CrA) copolymers are shown in Figure 2. The

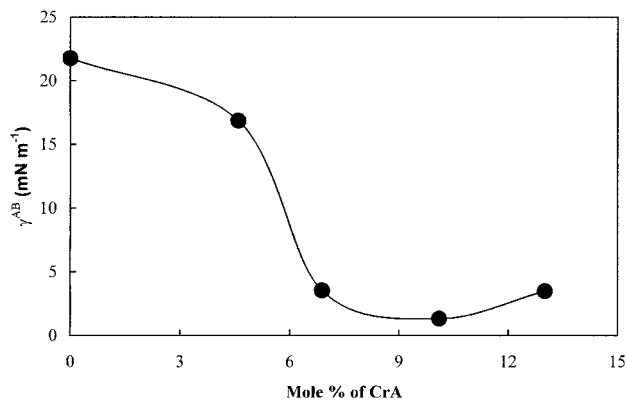


Figure 3 The variation of polar Lewis acid–base component of a solid surface free energy (γ_S^{AB}) with the amount of CrA (mol %) in the copolymer.

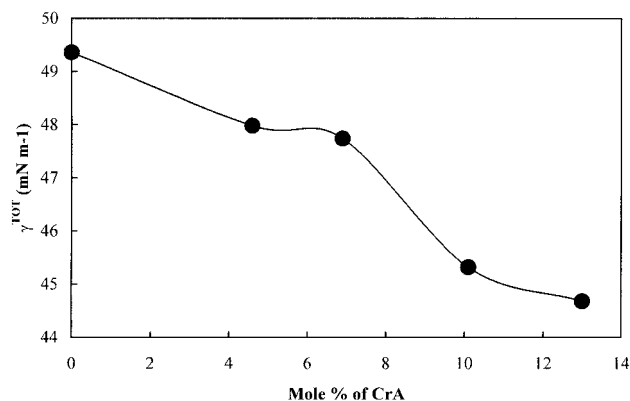


Figure 4 The variation of the total surface free energy of a solid (γ_S^{TOT}) with the amount of CrA (mol %) in the copolymer.

figure shows that the γ_S^{LW} was first sharply increased when the percentage of CrA increased from 0 to 6.9 mol % and then remained almost constant between 10.1 and 13.0 mol % CrA in the copolymer. This behavior can be explained on the basis that chains containing CrA have a lower dispersion force than chains containing VP. In contrast, the determining factor in the wettability variation of these copolymers arises as a result of AB interactions. The acid component of the solid at the interface interacts with the base component of the liquid; therefore, these interactions, some of which are numerically small, may be the determining factor in the wettability of the copolymers. The changes of the Lewis AB component of the surface free energy (γ_S^{AB}) with the CrA content of the copolymers are shown in Figure 3. As seen in the figure, the γ_S^{AB} was first considerably decreased and then remained almost constant with the CrA increase in the copolymer. This decrease reflected the decrease of the total surface energy (γ_S^{TOT}) with the increase of the CrA content, as reflected in Figure 4. This considerable decrease of both γ_S^{AB} and γ_S^{TOT} with the increase of CrA in the copolymer is probably due to the electron acceptor–donor interactions between the carbonyl groups of the VP units and the carboxylic acid groups of the CrA units in the backbone chain.

The authors thank Prof. E. Bayramli for providing laboratory facilities and for helpful discussions and the Gazi University Research Fund for the support of this work.

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