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pH-sensitivity of swelling of polyurethane crosslinked polyacrylate network

Mei Xuan Yu* and Wen Hua Zhang

Department of Applied Chemistry, Tianjin University, Tianjin 300072, China

SUMMARY

A pentacomponent acrylate copolymer containing hydroxyl and carboxyl groups was grafted with a semi–blocked polyurethane prepolymer and then deblocked to get polymer network with carboxyl groups. The network polymer can swell at pH range 6–13 and swell has reversible characteristic up to pH 11.Moreover, swelling kinetics is belong to a non–Fickian type.

INTRODUCTION

Intelligent polymers are currently being investigated world–wide, owing to their theoretical significance and practical potential. They are characterized by stimuti sensitivity. Their unique properties have spawned a broad spectrum of potential application based on responsibility to changes in environment. There is no report on intelligent polymer based on polyacrylate in litertatures. In consideration of responsibility of surface composition to change in substracte of polyurethane [1] . In this paper polyacrylate and the swelling behavoir was studied.

EXPERIMENTAL

Polymer network synthesis [2]

Acrylate copolymer (1) was prepared from a comonomer mixture of methyl methacrylate (MMA),ethyl acrylate (EA),

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*Corresponding author

hydroxyethyl acrylate (HEA), butyl acrylate (BA) and acrylic acid (AA) at molar ratio of MMA / EA / HEA / BA / AA =3.0 / 2.5 / 0.86 / 1.2 / 2.8 via benzoyl peroxide initiated polymerization in methyl ethyl ketone (MEK) at 84℃ for 5hrs.

Meanwhile, a polyurethane prepolymer(2) was synthesized from toluene diisocyanate (TDI) and linear poly(propylene oxide) polyether PPO–1000 (with Mn = 1000) at–NCO / –OH ratio being 2.1 : 1 in MEK. When the –NCO content of prepolymer was reached to 4.5%, the calculated amount of acetoxime was added and maintained reaction at 50℃ . So the semi–blocked polyurethane prepolymer(3), was obtained.

While, poly(acrylate–g–urethane) (4), was formed through the reaction of polyacrylate (1) with the semi–blocked prepolymer (3) at 50℃ for 3hrs.

Finally, a crosslinked polymer network (5) was produced by deblocking the casted graft polymer membrane (3) at 110℃ for 20–30 mins.

Methods

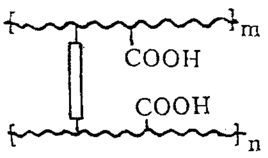
I.r. studies. I.r. spectra were recorded on a NICOLET 5DX–F TIR spectrophotometer. A thin polymer film specimen was obtained by casting with its MEK solution.

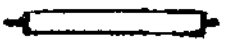
Swelling measurement. The polymer network (5) specimens were characterized by their equilibrium degree of swelling (the ratio of swollen weight / the equilibrium weight of swollen sample). Disc specimens with diameter / thickness (7.81mm / 0.53mm) being greater than 10 were cut from the polymer network membrane (5). The specimens were swollen in buffer solutions with an ionic strength of 0.1 in various PH at 37℃ .

The reversibility of swelling was determined as well. Sample was first swollen in a solution of pH = 11 and the degree of swelling was measured vs. time for 1hr, then the sample was transferred to a solution of pH = 5 and the swelling vs. time was estimated for 2 hrs. again. Experiment is carried out alternatively.

RESULTS AND DISCUSSION

The polymer network (5) studied has the formula,



where polyacrylate moieties [] containing carboxyl group are crosslinked by polyurethane block[].

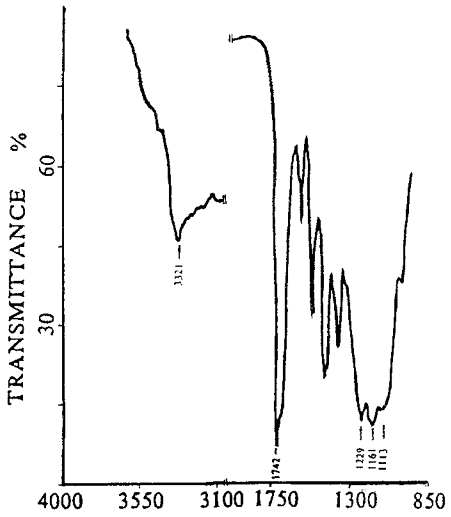


Figure 1 IR spectrum of polyurethane crosslinked polyacrylate network(5)

Fig. 1 shows the I R spectrum of the polymer network (5). The charateristic peak assignments are listed in Table 1.

Table 1. Infrared peak assignments for network 5

Peak, wavenumber(cm^{-1})	assignment
3321	OH str.
1742	c=o str.
1229	c–o (of carboxyl)
1160	c–o (in ester)
1113	c–o (in ether)

1. Swelling Behavoir

The pH dependence of swelling is displayed in Figure 2. Data indicate swelling initiates from pH > 6 and enhances slightly as pH raises to 9 (region Ⅰ). Then the degree of swelling reaches a plateau in a pH range of 9 to ca. 10 (region Ⅱ). This is attributed to the changes in the interaction between polymer network (5) and aqueous medium. Because of multiple hydrogen bondings in the network containing urethane, ester, ether and carboxyl groups will not swell unless the carboxyl group forms salt and hydrogen bonding dissociates at pH ca. 7. Changes in i.r. spectra of drying network specimen swollen in pH 9 indicate that the peak assigned to OH stretching of carboxy reduces and peak for ammonium of carboxylic at 1406cm^{-1} appears.

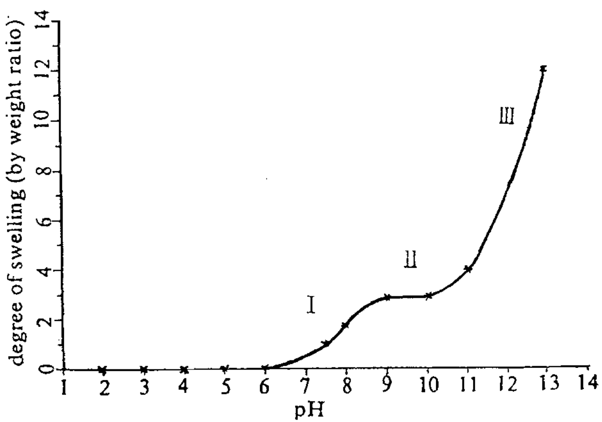


Figure 2 The pH dependence of the equilibrium degree of swelling for the polymer network

Swelling increases with pH obviously at pH > 11 (region Ⅲ in Figure 2) that is related to saponification of ester groups in polyacrylate moiety to carboxylic salt. Enhancements in 1514cm^{-1} (carboxylic salt) and 1230cm^{-1} (c–o in carboxyl) and reduction in 1160cm^{-1}(c–o in ester) in i.r. spectra of polymer network sample swollen at pH 13 that reveals the essential.

2. Reversibility of pH dependence swelling

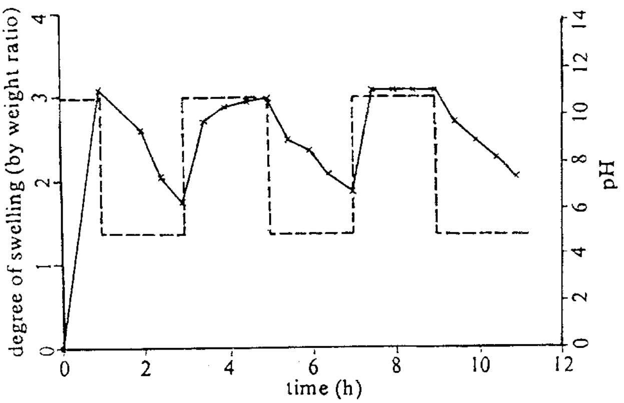


Figure 3 The degree of swelling as a function of time following changes in pH.

The reversibility of swelling of network sample is illustrated in Figure 3. In pH = 11 carboxyl groups within the polymer network dissociates and results in swelling. While at pH = 5 the ionized carboxyl groups can revert to carboxyl groups which leads to association of hydrogen bonding in the network accompanied by deswelling. The process is reversible.

3. Water sorption kinetics

The weight change of water sorption data are fitted to the Fickian equation,

$$M_t / M_\infty = 1 - \sum_{n=0}^{\infty} [8 / (2n+1)^2 \pi^{-2}] \times exp[-(2n+1)^2 \pi^2 (D_p t / L^2)]$$

where M_t and M_∞ is the weight absorbed at time t and at equilibrium, D_p is the polymer–fixed reference frame diffusion coefficient, which L represents the initial thickness of the sheet with aspect ratio greater than 10 : 1 [3] .

As shown in Figure 4 the swelling curve is sigmoidal when plotted against the square root of time and swelling deviates significantly from Fickian behaviour. This could be due to an initially retarded swelling rate caused by the original low water content of the more compact network and the dominance of the polymer–polymer interactions in this state. The diffusive rearrangement of segments in the polymer network needs relaxation time. Here comes both diffusion and relaxation controlled process.

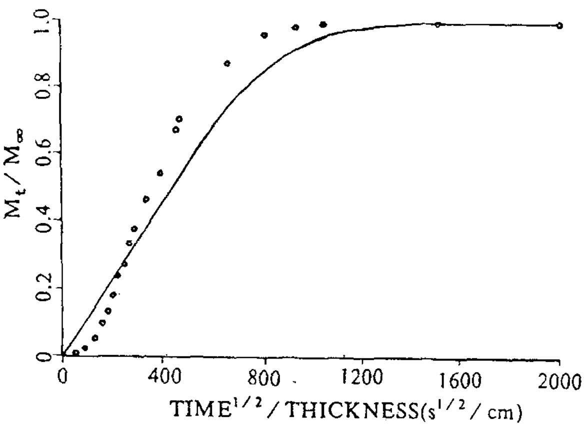


Figure 4 Swelling kinetics for the polymer network (5) specimen in pH 11 at 37℃.

CONCLUSIONS

Anionic charged polyacrylate polymer network can be synthesized by coupling with polyurethane prepolymer. The network shows a pH dependence swelling behaviour, owing to association—dissociation balance of hydrogen bonding dealing with protonized and ionized form transformation of carboxylic groups in response to changes in pH of medium.

References

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3. B.G.Kabra, M.K.Akhtar and S.H.Gehrke. Polymer, 33[5], 990(1992).

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