

# Studies on Water-Swellable Elastomer. I. Synthesis and Characterization of Amphiphilic Polymer

ZHIYUAN XIE,\*<sup>1</sup> MIN LI,<sup>1</sup> XINFANG CHEN,<sup>1</sup> HUIZHEN HU,<sup>2</sup> and SHUHUA LI<sup>2</sup>

<sup>1</sup>Institute of Materials Science, Jilin University, Changchun 130023, China, and <sup>2</sup>Polymer Physics Laboratory of Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun 130022, China

## SYNOPSIS

A new amphiphilic polymer i.e., polyethylene glycol (PEG) grafted crystalline neoprene, which was used as compatibilizer to improve the compatibility of elastomer and water-absorbent resin, has been investigated. The synthesis was based on the reaction between chlorine in neoprene and sodium salts of PEG. PEGs with molecular weights of 600 and 2000 were used. The grafting percent and the PEG content were calculated through elemental analysis of chlorine in the resulted copolymers. The maximum grafting percent of copolymers was ca. 24.80%. The molecular parameters such as number-average molecular weight and the average number of grafting chains on one CR backbone were also calculated and discussed. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Recently, many studies<sup>1,2</sup> on water-swellable elastomers have been reported. Water swellability can be imparted to hydrophobic rubber by physical or chemical methods. One method of producing water-swellable elastomer was mixing rubber with water-absorbent materials, such as crosslinked poly(vinyl alcohol), crosslinked polyacrylate, crosslinked starch-acrylate copolymer, and water-swellable urethane resins. But the disadvantages of physical mixing method, however, is that the water-absorbent materials are easily separated off. To enhance the compatibility between rubber and water-absorbent resin, amphiphilic polymers can be added to the mixtures.

An important synthesis method of amphiphilic polymer was chemical grafting. Soebianto and Yoshii<sup>3,4</sup> synthesized hydrophilic elastomer by radiation grafting of acrylic acid (AAc) onto ethylene-propylene rubber. Only a few examples were reported in which amphiphilic polymers were obtained by chemical modification. It was necessary for a polymeric backbone to have reactive groups (for grafting of hydrophilic chains onto hydrophobic rub-

bers by chemical modification), such as grafting copolymerization of *N,N*-dimethylacrylamide onto natural rubber,<sup>5</sup> grafting of poly(ethylene oxide) onto chlorosulphonated polyethylene and grafting of poly(ethylene oxide) onto butyl rubber.<sup>6</sup> The advantage of chemical modification over free radical graft copolymerization is that the molecular structure of polymer backbone and branched chains is well defined, so that the molecular parameters of these copolymers can be obtained and can be related to the physical properties. Neoprene is a highly versatile elastomer having a combination of properties suitable for many various applications and resisting deterioration by oils, solvents, weather, oxygen, ozone, heat and flame, etc. In this paper, water-soluble polyethylene glycol (PEG) was grafted onto the crystalline chloroprene rubber (CR-*g*-PEG) to improve the compatibility and the strength of water-swellable elastomer. The molecular characterization of copolymer (CR-*g*-PEG) was also given.

## EXPERIMENT SECTION

### Reagents

Neoprene (LDJ240) was supplied by Sichuan Chemical Industry Co. Ltd. (Chengdu, China); its number-average molecular weight determined by membrane osmometry is  $6.9143 \times 10^4$ , and its num-

\* To whom correspondence should be addressed.

ber-average degree of polymerization is  $7.81 \times 10^2$ . Polyethylene glycol with molecular weights 600 and 2000 (abbreviated PEG600 and PEG2000) were supplied by Beijing Chemical Factory (Beijing, China). Their molecular weight distribution was monodispersed ( $M_w/M_n < 1.1$ ).

Sodium and methanol of commercial origins were used without purification. Toluene was dried over sodium with stirring and distilled before use. Water was purified by the ion-exchanger and distillation. Other solvents were used as commercially supplied.

### Synthesis of Chloroprene Rubber Graft Polyethylene glycol (CR-g-PEG)

All reactions were carried out according to the following procedure. Water was separated as toluene azeotrope from the solution of PEG600 (12 g,  $[\text{OH}] = 0.04$  mol) in 80 mL of toluene. When 20 mL of toluene was removed, sodium (0.092 g,  $[\text{Na}] = 0.004$  mol) was added to this solution. The metallation of hydroxyl group in PEG was carried out under reflux with stirring for 12 h under nitrogen at  $115^\circ\text{C}$ . The reaction solution became dark brown. This reaction mixture was used in the next procedure. In a 250-mL four-necked round-bottomed flask, the solution of neoprene (4 g,  $[\text{Cl}] = 0.045$  mol) in 150 mL toluene was added. Water was separated as toluene azeotrope in the same way, and 20 mL of toluene was removed from this solution. The dark-brown solution of sodium alkoxide derivative of PEG was added dropwise, and the reaction mixture was stirred vigorously at 75, 85, 95, and  $110^\circ\text{C}$  in an oil bath under nitrogen for the prescribed time. The reaction mixture was poured into a large amount of methanol and reprecipitated three times from toluene solution with methanol to remove the unreacted PEG. Soxhlet extraction with methanol was also carried out for 24 h. The resulted polymer was dried in vacuum at room temperature. The route of synthesis was given in Scheme 1.

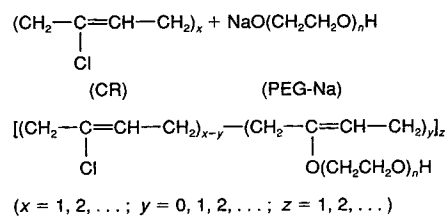
### Measurement

IR spectra were recorded on a Nicolet-5DX spectrometer. Number-average molecular weights were measured by membrane osmometry.

## RESULTS AND DISCUSSION

### Characterization of PEG-Na

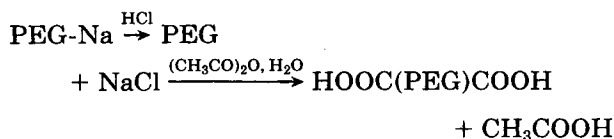
PEG600 and PEG2000 were supplied by Beijing Chemical Factory. Their molecular weight contri-



Scheme 1. Synthetic route of CR-g-PEG.

bution were ranged from 580 to 620 and from 1850 to 2150, respectively.

The reaction between PEG and sodium was carried out under nitrogen without water, so PEG's molecular weight should not be changed. The molecular weights of PEG-Na were measured by titration method as follows:



So the molecular weight of PEG could be calculated from the acid concentration in solution, which was measured by titration method. The measured molecular weights of PEG-Na were 573 and 1852, which showed that the PEG molecular weights in PEG-Na were not changed. In the following calculation, PEG's average molecular weights of 600 and 2000 were used.

### Characterization of CR-g-PEG

The molecular structure of the copolymers (CR-g-PEG) was evaluated by IR spectroscopy. IR spectrum of CR-g-PEG600 with a grafting percent of 26.51% is shown in Figure 1. It can be seen that the absorption band due to the aliphatic C—O—C stretching vibration of the ether group is detected at  $1113\text{ cm}^{-1}$ , the O—H stretching vibration of hydroxyl group of PEG at  $3400\text{ cm}^{-1}$ , as well as the C=C stretching vibration band of chloroprene rubber at  $1665\text{ cm}^{-1}$ . For the mixture of chloroprene rubber and PEG prepared by precipitating it in toluene with methanol, neither stretching vibration band of hydroxyl group nor that of ether group was detected in its IR spectrum. From the above analysis, the proposed molecular structure of graft copolymers was confirmed.

### Effect of Reaction Conditions on the Grafting Percent and PEG Content in Graft Copolymers

Because the synthesis was based on the reaction between chlorine in CR backbone and sodium salts of

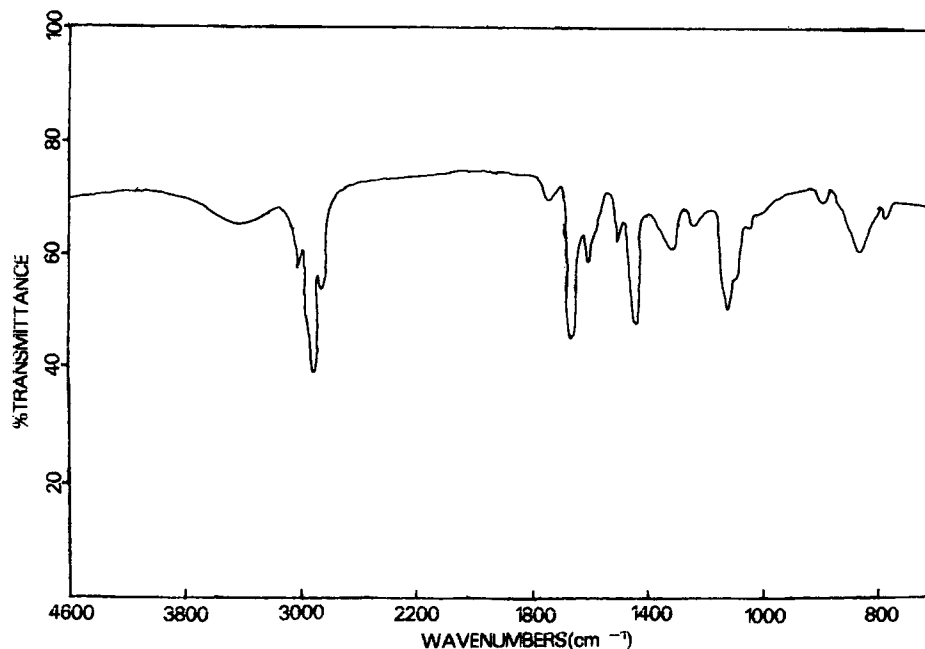


Figure 1 IR spectrum of graft copolymer CR-g-PEG (sample no. 13).

polyethylene glycol, the degree of reaction, the grafting percent, and the PEG content in graft copolymers can be estimated by measuring the weight percent of chlorine element in the resulting copolymers. The elemental analysis of chlorine was done in Analytical Laboratory of Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China. According to the proposed molecular structure of graft copolymers, the weight percent of chlorine element can be described as in eq. (1).

$$\text{Wt \% of Cl} = \frac{(\text{atomic wt of chlorine} \times (1 - P_A) \times 100) / [\text{molecular wt of monomer unit of neoprene} \times (1 - P_A) + (\text{molecular wt of PEG} + \text{molecular wt of butadiene} - 1) \times P_A]}{1} \quad (1)$$

where  $P_A$  is the degree of reaction that can be obtained and so that the graft copolymer composition. The grafting percent and PEG content in graft copolymers are defined by eqs. (2) and (3).

$$\text{Grafting percent} = \frac{\text{Wt of PEG grafted} \times 100}{\text{Wt of neoprene backbone}} \quad (2)$$

$$\text{PEG content} = \frac{\text{Wt of PEG grafted} \times 100}{\text{Wt of graft copolymer}} \quad (3)$$

Effect of reaction time on grafting percent and PEG content is shown in Table I. It can be seen that the grafting percent and PEG content increase with increase of reaction time.

The results of graft copolymerizations, which were carried out at 75 and 85°C for 2 and 10 h while

Table I Effect of Reaction Time on Graft Copolymerization of PEG onto Neoprene

Sample No.	Neoprene (g)	PEG			Grafting Reaction			Grafting Percent (%)	PEG Content (%)
		$M_n$	Wt (g)	Na (g)	Temperature (°C)	Time (h)	Chlorine (wt %)		
1	4	600	12	0.092	75	2	40.92	—	—
2	4	600	12	0.092	75	5	37.86	5.42	5.16
3	4	600	12	0.092	75	10	37.48	6.39	6.03
4	4	600	12	0.092	75	13	36.15	9.93	9.08
5	4	2000	20	0.049	85	2	38.53	4.00	3.84
6	4	2000	20	0.049	85	5	37.76	6.05	5.71
7	4	2000	20	0.049	85	9	37.21	7.57	7.05

**Table II** Effect of Reaction Temperature on Graft Copolymerization of PEG onto Neoprene

Sample No.	Neoprene (g)	PEG		Grafting Reaction			Chlorine (wt %)	Grafting Percent (%)	PEG Content (%)
		$M_n$	Wt (g)	Na (g)	Temperature (°C)	Time (h)			
1	4	600	12	0.092	75	2	40.92	—	—
3	4	600	12	0.092	75	10	37.48	6.39	6.03
9	4	600	12	0.092	85	2	37.85	5.45	5.18
10	4	600	12	0.092	85	10	35.76	11.00	9.97
11	4	2000	20	0.049	75	2	41.67	—	—
12	4	2000	20	0.049	75	10	37.64	6.38	6.00
5	4	2000	20	0.049	85	2	38.53	4.00	3.84
7	4	2000	20	0.049	85	9	37.21	7.57	7.05
13	4	600	12	0.092	110	5	30.85	26.51	21.22
14	4	600	12	0.092	110	10	31.26	24.71	20.05

keeping other reaction parameters constant, are given in Table II. It can be seen that the grafting percent and the PEG content in the copolymers increase with reaction temperature. The higher the reaction temperature, the larger the grafting percent and PEG content. But for the case of higher reaction temperature, such as 120°C or higher, the intermolecular cross-linking reaction of CR backbone may occur. Under the conditions of the same reaction time and temperature but different graft chain length, the grafting percent for grafting short-side chain onto CR is higher than that for long-side chain grafting.

#### Calculations of Molecular Parameters of Graft Copolymers

Because of the well-defined backbone and grafted PEG of graft copolymers, the number-average molecular weight of graft copolymers and the average number of grafts on one chloroprene rubber backbone can be calculated by the following equations:

$$M_n = P_A P_{n1} M_{n2} + M_{n1} \quad (4)$$

$$\sigma = P_A P_{n1} \quad (5)$$

where  $M_n$  is the number-average molecular weight of graft copolymers,  $M_{n1}$  and  $M_{n2}$  are the number-average molecular weights of chloroprene rubber and PEG, respectively;  $P_A$  is the degree of reaction;  $P_{n1}$  is the number-average degree of polymerization of CR; and  $\sigma$  is the average number of grafting chains on one CR backbone.

From eqs. (4) and (5), it can be seen that the molecular parameters of graft copolymers,  $M_n$  and  $\sigma$ , will be presented only as a function of  $P_A$  provided that the molecular weights of polymers backbone and PEG are known. Therefore,  $M_n$  and  $\sigma$  can be calculated by means of the determination of  $M_{n1}$ ,  $M_{n2}$ , and  $P_A$ . The results tabulated in Table III shows that  $M_n$  increase with increasing  $M_{n2}$  and  $P_A$ , and  $\sigma$  is only related to  $P_A$  under the same backbone condition.

#### CONCLUSION

Polyethylene glycol-graft-chloroprene rubber was synthesized by the reaction between chlorine in CR and sodium salts of polyethylene glycol. The reaction between sodium and hydroxyl group of PEG was controlled by controlling the molar ratio

**Table III** Molecular Parameters of Graft Copolymers Listed in Tables I and II

Sample No.:	2	3	4	5	7	9	10	12	13	14
$P_A$ (%)	0.75	0.89	1.38	0.14	0.33	0.78	1.52	0.28	3.68	3.43
$M_n$ ( $\times 10^4$ )	7.27	7.32	7.56	7.18	7.43	7.27	7.63	7.35	8.63	8.52
$\sigma$	5.88	6.93	10.76	1.36	2.53	6.06	11.93	2.17	28.74	26.79

For calculations:  $P_{n1} = 7.81 \times 10^2$ .

of Na and PEG to obtain the metallization of mono-hydroxyl group in PEG, which would reduce the cross-linking degree and improve the solubility of the resulting copolymers. The grafting percent and PEG content were calculated through elemental analysis of Cl. The grafting percent and PEG content increase with increase of reaction time and temperature and the maximum grafting percent of the resulting copolymers after the purification was ca. 26.51% and the PEG content of graft copolymers was ca. 21.22%. The molecular parameters were calculated and the results show that they are related to the reaction conditions as well as the properties of polymer backbone and graft chains.

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