

Synthesis of CO₂ Copolymer Based Polyurethane Foams

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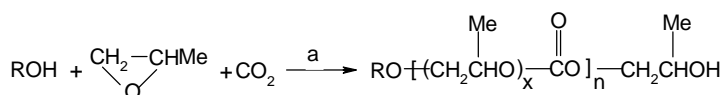
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Abstract: CO₂-copolymer based polyurethane foams were synthesized and characterized in this paper. The foams were found to have higher strength and lower heat of combustion than the conventional polyether polyurethane foams. They may find wide applications in many fields.

Keywords: CO₂, epoxides, aliphatic polycarbonates, polyurethane foams.

Aliphatic polycarbonate polyurethanes (PU) especially as elastomers have been developed. These materials have been found to have many particular properties and applications such as elastomers^{1,2} and coatings³. The suitable aliphatic polycarbonates are those having molecular weight of 10³ and have designed number (*i.e.*, 2 or 3) of OH end groups. Most of these polyols were synthesized by COCl₂ or R₂CO₃ methods⁴, where R is alkyl or aryl. Attempted preparation through CO₂-epoxide copolymerization generated resins with molecular weights either too high or too low and needed additional complicated treatments⁵. In addition, the “copolymer” consisted of very few CO₂ repeating units (carbonate fraction $f_c = 0.06 \sim 0.23$)^{5,6}. We have suggested a novel technique as regulated CO₂-epoxide copolymerization (**Scheme 1**), by which aliphatic polycarbonate polyols with carbonate fractions as high as 0.3 ~ 0.45 and molecular weights (viscosity averaged) of 4000 ~ 10000 can be easily produced⁷. Further, we reported the synthesis of polyurethane elastomers and polyurethane interpenetrating networks based on this kind of polyols^{1,8}. In this paper we report the synthesis of PU foams from the regulated copolymers of CO₂ and propylene oxide (PO).

Scheme 1



a: In the presence of PBM catalyst, polyol resins may be obtained if R consisted of more than one OH groups

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According to **Scheme 1**, the polyol preparation was carried out in a 5 L autoclave, in which were charged CO₂ 1100 g, PO 2.5 L, dipropylene glycol 0.05 L, a polymer supported bimetallic catalyst (PBM)⁹ 20 g. After reaction at 60°C for 12 h, the obtained resin was washed with 2 L hot water then vaporized at 60°C under 1300 Pa vacuum for 2 h to remove the unreacted PO and the by product propylene carbonate (PC), yielding about 900 g of the copolymer polyols. Content of residual water was determined by ASTM D2849. Viscosity averaged molecular weight of the copolymer was 8030 according to reported method¹⁰. IR spectra of the copolymers showed characteristic signals at 1745, 1250 and 790 cm⁻¹, for the carbonate and ether groups. ¹H NMR integration showed that the f_C of the copolymers were around 0.37.

CO₂ copolymer PU foams were prepared by the reaction of the so obtained polyols with diisocyanates such as carbodiimide modified 4,4'-diphenylmethane diisocyanate (C-MDI). The foaming process was conducted by one-step blowing method⁸ at room temperature while stirring at a rate of 1600 r/min. Composition of the reactants for some experiments was listed in **Table 1**. After blowing was finished the foam was matured at 60°C for 48 h.

Properties of foams were measured by standard methods: GB6343-86, GB6344-88, GB9641-88, GB8812-88. Strength and modulus were measured on a XLL-50 universal testing machine. Some results were listed in **Table 2** for comparison with other PU foams^{11,12}. The obtained foams were considered to belong to semi-rigid category and have higher strengths than common PU foams with similar density. Because the polycarbonate based PU is rich of CO₂ structural units (about 17wt %), it can be readily made flame retardant. If the polycarbonate polyols were made of CO₂ and ethylene oxide, the PU foams from them had excellent biodegradability.

Because CO₂ as a monomer and the PBM catalysts are not expensive, the costs of manufacturing CO₂-copolymer based PU foams, in large scale, may be lower than common PU foams.

Table 1 Composition of raw materials (g) for preparation of PU foams

Sample No.	383	381	272	262
PPC	100	100	100	100
Propanetriol	6	6	6	6
Water	3.3	2.6	2.0	1.6
Dabco-33LV	0.6	0.6	0.6	0.6
Tin cat. ^a	0.16	0.16	0.16	0.16
Silicone surfactant	1.5	1.5	1.5	1.5
Isocyanate index	1.1	1.1	1.1	1.1

a): 6.3% dibutyltin dilaurate in toluene

Table 2 Properties of PPC-PU foams and some reported foams^{11,12}

Sample	383	381	272	262	a ¹¹	b ¹²	c ¹²
Density kg/m ³	42	56	89	115	55-65	<250	60±5
Tensile strength KPa	230	270	460	600	130-170	≥150	110
Crack elongation%	33.6	23.6	19	17.2	14-18	130±80	67
Bending strength KPa	167	180	473	670	-	-	-
25%compression strength Kpa	100	113	367	567	50-60	≥20	55±5

a): general semi-rigid PU foams. b and c): some polyether based semi-rigid PU foams.

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References

1. H. Peng, X. X. Lin, B. Huang, *Chemical World* (in Chinese), **1995**, 8, 426.
2. R. F. Harris, M. D. Joseph, C. Davidson, C. D. Deporter, V. A. Dais, *J. Appl. Polym. Sci.*, **1990**, 41, 487.
3. T. Matsuura, Y. Irie, *Mokuzai Kogyo*, **1999**, 54 (7), 318.
4. W. Kuran, *Polymeric Materials Encyclopedia*, Ed. by Joseph C. Salamone, CRC press, Inc., Boca Raton, **1996**, 9, p6623.
5. R. F. Harris, *J. Appl. Polym. Sci.*, **1992**, 44, 605.
6. J. Kuyper, P. W. Lednor, G. A. Pogany, *US Patent*, 4826953, **1989**.
7. L. B. Chen, B. Huang, *Chin. Patent*, ZL, 91109459, **1991**.
8. L. B. Chen, S. Y. Yang, X. X. Lin, *Polymers for Advanced Technologies*, **2001**, 12, 687.
9. S. H. Chen, L. B. Chen, X. X. Lin, *Chin. Patent*, ZL, 89100701, **1989**.
10. L. B. Chen, E. J. Ni, S. Y. Yang, *Journal of Instrumental Analysis* (in Chinese), **1995**, 3, 24.
11. X. D. Li, S. Q. Zhang, *Polyurethane Industry* (in Chinese), **2000**, 15 (1), 45.
12. X. J. Li, *Polyurethane, Handbook of Plastic Industry*, Chemical Industry Press, Beijing, **1999**, p. 217.

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