Experimental Section

Materials

Furfuryl alcohol and tetrahydrofurfuryl alcohol were distilled before use. N-phenyl maleimide was recrystallized in ethanol. Glycerine was analytically pure and distilled under reduced pressure before use. Yttrium trichloroacetate \([Y(CCl_3COO)_3]\) and diethyl zinc \((\text{ZnEt}_2)\) were synthesized according to the literature.\(^{1,2}\) Commercial \(\text{CO}_2\) (99.99% pure) and other materials were used without further purification.

Monomer synthesis

Furfuryl glycidyl ether (FGE) was synthesized by etherification of epichlorohydrin with furfuryl alcohol (FA) using phase-transfer catalyst. To a 1000 ml 50% aqueous solution of \(\text{NaOH}\) was added 12 mol epichlorohydrin and 0.04 mol tert-butylammonium sulfate under stirring in ice-water bath, 4 mol furfuryl alcohol was then added dropwise while keeping the temperature below 15 °C. After stirring for another 3 hours below 15 °C, the organic layer was washed with saturated brine to
neutral and dried over magnesium sulfate. The organic products were purified by vacuum distillation and further purified by vacuum rectification. The product (75% yield with respect to furfuryl alcohol) was dried over CaH₂, distilled, and stored under argon on molecular sieves (4Å). Tetrahydro-furfuryl glycidyl ether (TFGE) (70% yield with respect to tetrahydrofurfuryl alcohol) was synthesized from epichlorohydrin and tetrahydrofurfuryl alcohol in similar condition. The purity of FGE or TFGE was higher than 99.5% as determined by GC/MS.

**Preparation of copolymer**

Rare earth ternary coordination catalysts (Y(CCl₃O)₃-ZnEt₂-glycerine) were prepared under argon atmosphere according to literature. The freshly prepared catalyst suspension in calculated amount of FGE (or TFGE) was introduced into a 150 ml autoclave free of oxygen and water. Copolymerization was carried out at designed pressure and temperature. After a certain period, the copolymerization was terminated by addition of methanol solution containing 5% dilute hydrochloric acid. The copolymer of FGE and CO₂ was dissolved in CH₂Cl₂, and stored under argon. The copolymer of TFGE and CO₂ was dried in vacuum at 40 °C till constant.

**Addition of antioxidant into the copolymer**

Calculated amount of antioxidant was added to the solution of FGE and carbon dioxide copolymer in dichloromethane solution and stirred for 1 hour. After evaporation of the solvent, the solid was dried in vacuum at 40 °C to remove the solvent thoroughly.

**DA reaction in copolymer of FGE and CO₂**
The copolymer of FGE and CO\textsubscript{2} as well as N-phenyl maleimide (molar ratio of N-phenyl maleimide to furan ring was 1:1, 3:1 and 4:1) was dissolved in 50 ml dichloromethane and heated under reflux in a nitrogen atmosphere for 24 hours. The resulting products were precipitated by methanol, redissolved in dichloromethane, reprecipitated in methanol, and then dried in vacuum at 40 °C till constant.

**Measurements**

All the products were freshly produced and dried in vacuum at 40 °C for 1 hour before test. \textsuperscript{1}H NMR spectra of the products were recorded at room temperature on a Bruker AV-300 NMR spectrometer using CDCl\textsubscript{3} as the solvent and tetramethylsilane as internal reference. The molecular weight and polydispersity of the copolymer were determined on a Waters 410 gel permeation chromatography at 30 °C in polystyrene standard using dichloromethane as eluent. The glass transition temperature (\(T_g\)) was determined with a PerkinElmer 7 differential scanning calorimetry (DSC) instrument. Infrared (IR) spectra were recorded on an Elmer 983 spectrophotometer. Purity of the monomer was measured with Agilent GC/MS 5975/6890N. Elemental analysis was performed on Vario EL.

The crosslinked products were extracted by dichloromethane at 40 °C in a Soxhlet apparatus for 24 h, the insoluble part was completely dried in vacuum, and the gel content was calculated from weight percentage of the dried gel in initial polymer.
Figure 1. IR spectra of PFGEC (a), DA reaction products (b and c), the molar ratio of N-phenyl maleimide to the furan ring was 1:1(b) and 3:1(c), respectively.

Figure 2. IR spectra of the TFGE (a), and PTFGEC (b).

Figure 3. $^1$H NMR spectra of the TFGE (a), and PTFGEC (b).
References:


