Experimental Section

Materials. Propargyl bromide (Aldrich Chemicals, 80% solution of toluene) was dried over calcium hydride and fractionally distilled. Molybdenum(V) chloride (Aldrich Chemicals Co., resublimed 99.9%) and tetra-n-butyltin were used without further purification. All solvents were used after purification according to conventional methods. Special care was taken to ensure complete removal of moisture and oxygen. Carbon dioxide (99.99% purity) was obtained from Shinyang Oxygen Co. (Seoul, Korea), 1,1,1,2-tetrafluoroethane (R134a) (99.95% purity) from Allied Signal (Baton Rouge, LA), and dimethylether (DME) (99+% purity) from Aldrich Chemical Co. (Milwaukee, WI). They were used as received without further purification. All chemicals used were reagent grade (Aldrich) and purified by the ordinary methods (Perrin, D. D.; Armarego, W. L. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988). Dimethyl malonate (27g) was added to dry ethanol (150 ml) containing sodium ethoxide (7.8g) (Aldrich Chemical Co, 96%). After 5 min, propargyl bromide (42 g) was slowly added to the stirred suspension, and the mixture heated under reflux for 30min. After removal of the alcohol in a vacuum, the residue was diluted with water, and the neutral fraction was isolated and dissolved in hexane. DMDPM (33 g) slowly separated in octahedral: yield 79%; m.p. 45.5 °C. See Fig. S-1 for ^{1}H NMR spectrum of DMDPM.

Polymerization Procedure in Supercritical CO_2. Polymerization was conducted in a 30 mL stainless steel high-pressure cell equipped with a magnetic stirring bar, a nitrogen inlet, and an electrically heating mantle. DMDPM (1.56 g; 7.5 mmol of DMDPM) and $MoCl_5$ solution (1.5 mL of a 0.1 M solution in toluene; 0.15 mmol of $MoCl_5$) were added to the cell. After removing toluene under vacuum, the reactor was purged with nitrogen for 5 min, evacuated for 1 h using a liquid nitrogen cooled trap and then purged with nitrogen for an additional 10 min. The cell was then disconnected from the nitrogen line, evacuated, and connected to the CO_2 feed system. The cell was filled with liquid CO_2 by using an air-driven gas compressor (Maximator Schmidt Kranz & Co. GmbH), gradually heated to 40 °C to achieve 250 bar, and then polymerization was allowed to proceed for the predetermined time. After cooling the reactor down to room temperature, CO_2 was vented through a needle valve into chloroform, to collect both the unreacted monomer and polymer. To quantify the conversions of DMDPM, the cell was rinsed with chloroform to dissolve traces of polymer and monomer. Both of these chloroform solutions were then poured into a large volume of cold methanol, and the precipitated polymer was recovered by filtration and dried under vacuum at room temperature to constant weight. Monomer conversion was determined gravimetrically.

Polymer Characterization. Molecular weights (MWs) and molecular weight distributions (MWDs) were determined by gel permeation chromatography (GPC) using a Waters 510 fluid unit, a Waters 717 plus autosampler, and a Waters 410 differential refractometer with a combination of three Shodex microstyragel® columns with molecular weight exclusion limits of 1500/70000/400000 g/mol. The column was eluted with $CHCl_3$ (flow rate of 1.0 mL/min at 30 °C) and calibrated with polystyrene standards over a MW range of 1 000 – 350 000. NMR spectra were obtained at 500 MHz (^{1}H) and 125.7 MHz (^{13}C) on a Bruker Avance 500 in $CDCl_3$. Tetramethylsilane was used as an internal reference. FT-IR spectra were recorded on a Beckman DU-7B scanning spectrometer.

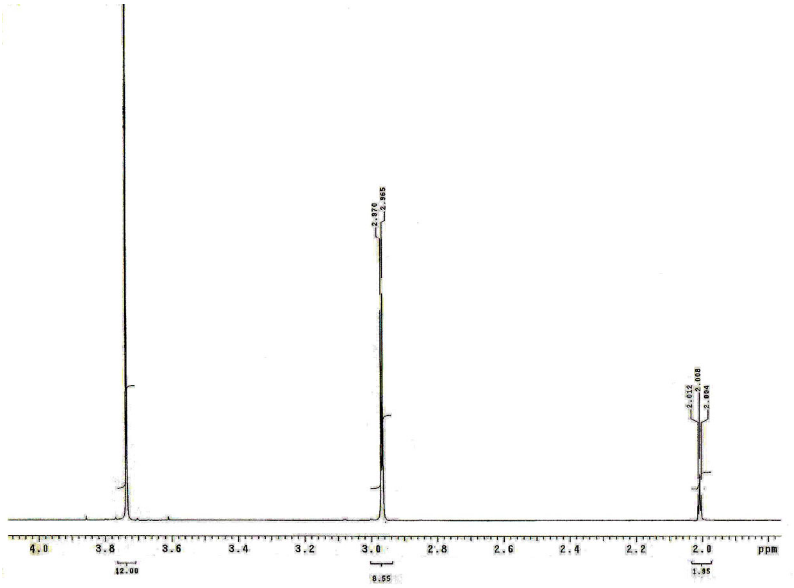

Fig. S-1 ^{1}H NMR spectrum of dimethyl dipropargylmalonate (measured in $CDCl_3$).

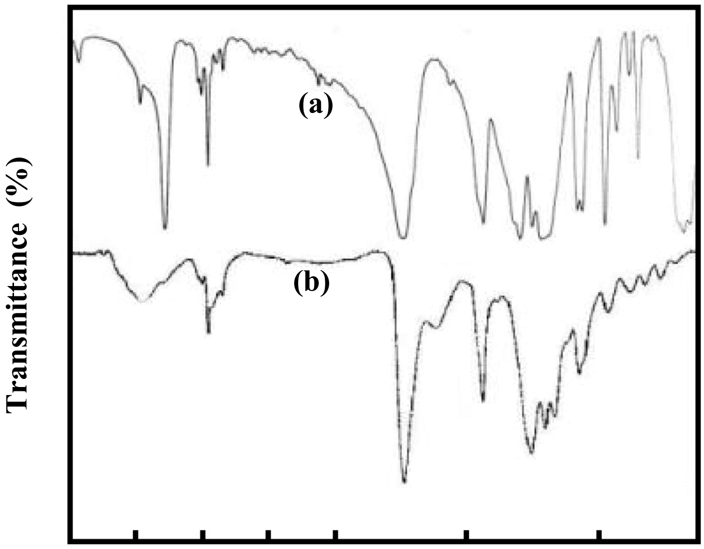

Fig. S-2 IR spectrum of (a) dimethyl dipropargylmalonate and (b) poly(dimethyl dipropargylmalonate) (sample: Table 1, no. 7, KBr pellet).

DMDPM. IR (KBr, cm^{-1}): 3288 (≡C-H stretch), 2970, 2203 (C≡C stretch), 1740 (C□O stretch), 1435 (C-H band), 1298, 1252, 1217, 1061, 974, 675 cm^{-1}.

Poly(DMDPM). M_n = 12 500; PDI = 2.05. IR (KBr, cm^{-1}): 3447, 2953 (C-H stretch), 1734 (C□O stretch), 1437 (C-H bend), 1256, 1202, 1167, 1113, 964 cm^{-1}.

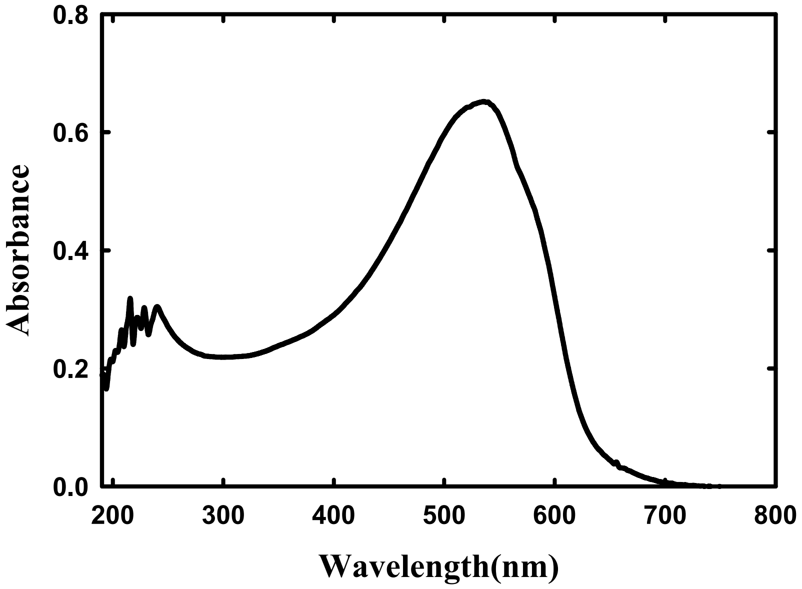

Fig. S-3 UV-visible spectrum of poly(dimethyl dipropargylmalonate) (sample: Table 1, no. 7, measured in THF)

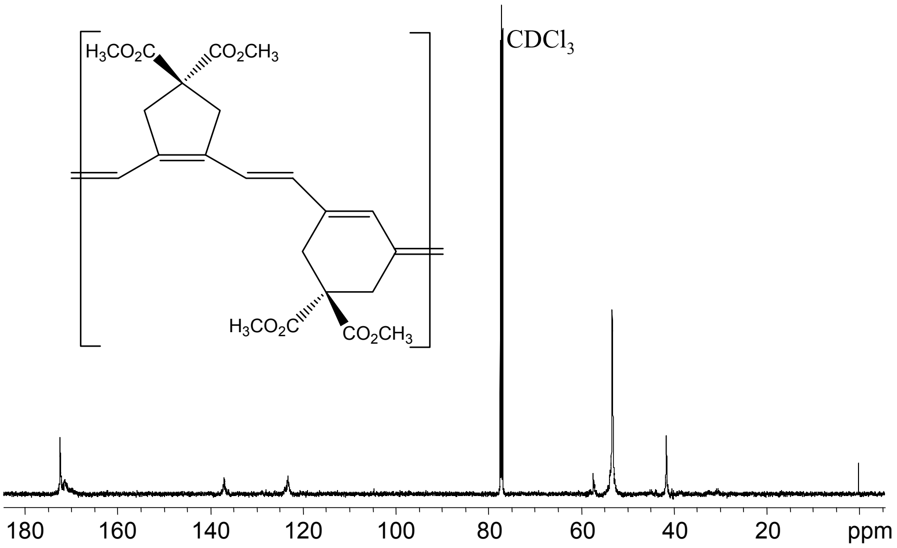

Fig. S-4 ^{13}C NMR spectrum of poly(dimethyl dipropargylmalonate) (sample: Table 1, no. 7, measured in $CDCl_3$): δ 172.5 (COO), 137.1 and 123.3 (C_{olefinic}), 57.4 (C_{ipso}), 53.3 (OCH$_3$), 41.7 (C_{allylic}).