

Synthesis of methacrylate monomer of 6CAM and polymerization

The synthesis for methacrylate monomer and polymerization are outlined in Scheme 1 in the text.

Monomer synthesis

4-(6-Hydroxyhexyloxy)cinnamic acid (6CA) was synthesized by the conventional Williamson synthesis from 4-hydroxycinnamic acid and 6-chlorohexane-1-ol in ethanol using KOH. After the reaction, unreacted starting materials were removed by washing with methanol, and the resultant crude products were purified by recrystallization from tetrahydrofuran (THF). Yield: 50-60 mol%. Mp. 176°C. ¹H-NMR (DMSO-d₆): δ (ppm) 1.32-1.42 (m, 6H), 1.66-1.70 (m, 2H), 3.4 (3H, overlapped with H₂O), 3.97 (t, J=6.4Hz, 2H), 4.38 (brs, 1H), 6.34 (d, J=15.9Hz, 1H), 6.93 (d, J=8.5Hz, 2H), 7.51 (d, J=15.9Hz, 1H), 7.59 (d, J=8.5Hz, 2H).

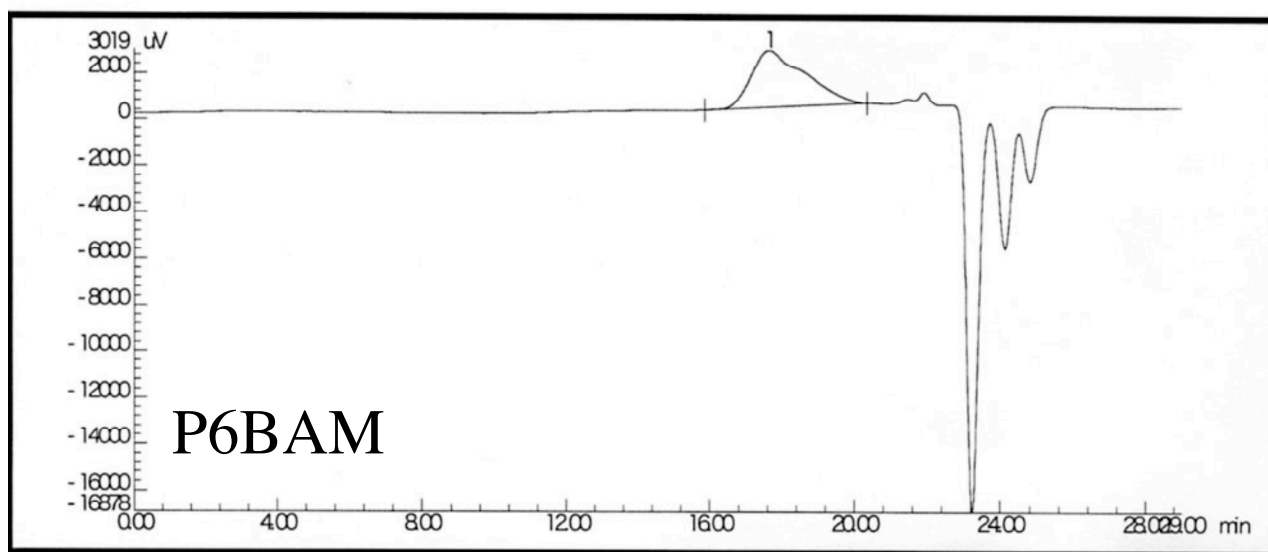
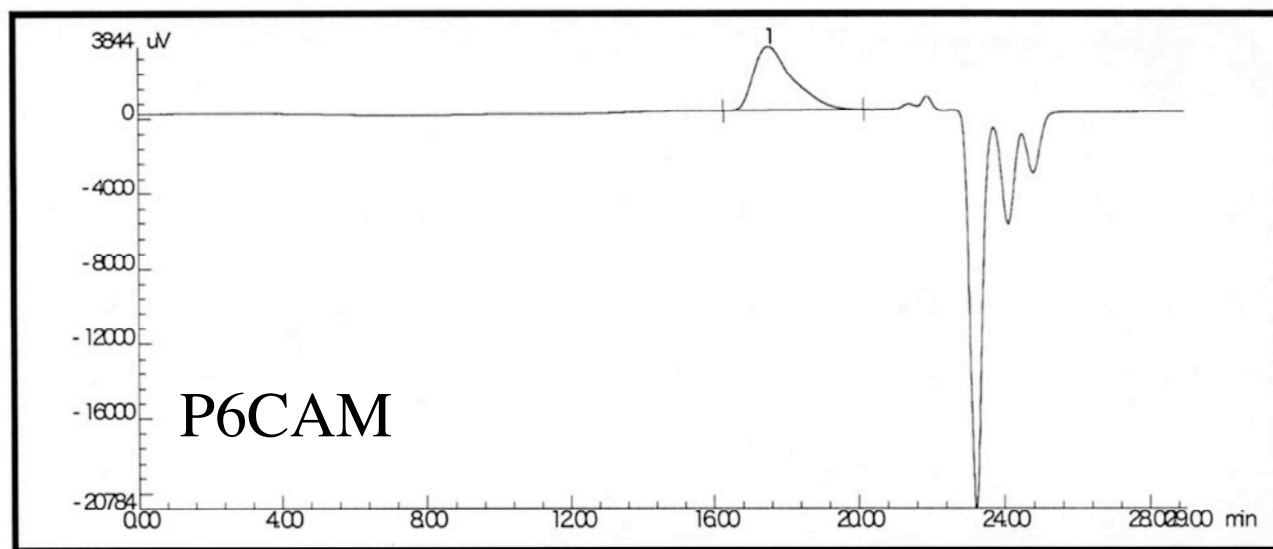
4-(6-Methacroyloxyhexyloxy)cinnamic acid (6CAM): A mixture of 10 g (37.8 mmol) of 6CA, 4.75 g (45.4 mmol) of methacryloyl chloride, 5.5 g (45.4 mmol) of *N,N*-dimethylaniline, and 10 mg of 2,6-di-*t*-butyl-4-methylphenol (inhibitor) in 50 ml of dioxane was heated at 65°C for 3h. After cooling, 50 ml of water was added and conc. hydrochloric acid was added dropwise. The precipitate solid was washed with water and purified by silica-gel column chromatography with ethyl acetate/*n*-hexane (7/3) as eluant. Then the product was recrystallized from THF-hexane mixture. Yield: 2.5 g (19 mol%). C 119°C N 123°C I. ¹H-NMR (CDCl₃): δ (ppm) 1.46-1.52 (m, 4H), 1.70-1.73 (m, 2H), 1.80-1.83 (m, 2H), 1.94 (s, 3H), 3.99 (t, J=6.4Hz, 2H), 4.16 (t, J=6.4Hz, 2H), 5.55 (s, 1H), 6.10 (s, 1H), 6.31 (d, J=16.0Hz, 1H), 6.89 (d, J=8.6Hz, 2H), 7.49 (d, J=8.6Hz, 2H), 7.74 (d, J=16.0Hz, 1H).

Polymer synthesis

P6CAM was synthesized by a radical polymerization of **6CAM** in THF solution using AIBN as the initiator at 55°C for 1 day. After the polymerization, the polymer was purified by reprecipitating several times from a THF solution to methanol and diethyl ether. The synthetic yield was 77 wt%. ¹H-NMR

(THF- d_8): δ (ppm) 0.96-1.96 (m, 13H), 3.8-3.9 (m, 4H), 6.28 (d, $J=16.0$ Hz, 1H), 6.88 (d, $J=8.1$ Hz, 2H), 7.45 (d, $J=8.1$ Hz, 2H), 7.57 (d, $J=16.0$ Hz, 1H). $M_n=25000$, $M_w=39000$.

GPC chart of synthesized polymers



IR Assignment

