Synthesis and Characterization of Novel Multiblock Copolymers Based on Polyurethanes Derived from 6-FDA-Glycol and Poly(dimethylsiloxane)

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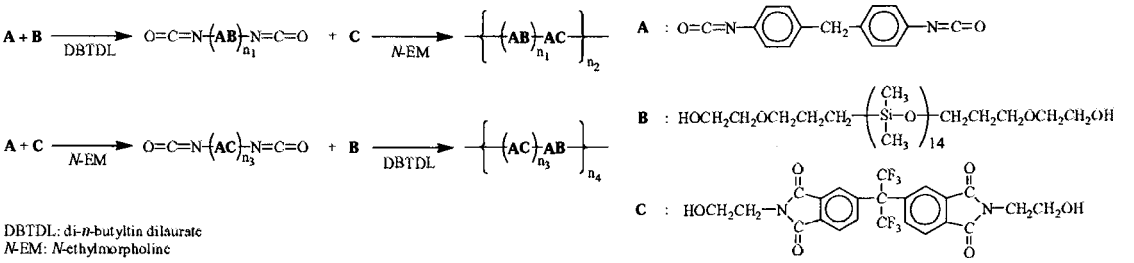
A novel class of hydrophobic block copolymer materials based on polyurethanes (PUs) derived from 4,4'-(hexafluoroisopropylidene)bis[*N*-(2-hydroxyethyl)phthalimide] (6-FDA-glycol, **C**) and poly(dimethylsiloxane) (PDMS) was developed. PU-PDMS multiblock copolymers of wide ranging compositions were successfully synthesized by solution polyaddition through two different procedures.



In the two-step method, α,ω-isocyanate terminated PUs, which were preformed by the reaction of 4,4'-methylene diphenylisocyanate (MDI, **A**) with 6-FDA-glycol in 4-methyl-2-pentanone, were subjected to polyaddition with α,ω-bis(3-aminopropyl)poly(dimethylsiloxane) (PDMS-glycol, **B**) in the same flask, leading to the formation of the multiblock copolymers. In the one-step method, three reaction components, 6-FDA-glycol, MDI, and PDMS-glycol, were reacted all together in 4-methyl-2-pentanone. High-molecular-weight multiblock copolymers having M_n values of 2.2-4.8 x 10^4 g/mol were obtained by these polymerizations. Calorimetric measurements showed that the PU-PDMS multiblock copolymer films obtained by the two-step method had better defined, microphase-separated morphology (**Fig.**) than those obtained by the one-step method. Regardless of the glycol components, they are highly soluble in a variety of solvents such as polar aprotic solvents, phenols, and chlorinated hydrocarbons and could be cast into transparent, ductile, and elastomeric films from the DMAc solutions. The mechanical properties of the multiblock copolymer films depended markedly on the 6-FDA-glycol content; at low 6-FDA-glycol levels the materials are analogous to thermoplastic elastomers, and at higher 6-FDA-glycol contents the materials behave as rubber-toughened polyimide plastics. These films all are very hydrophobic. The contact angles formed by water on the film surface were larger than 70° and increased monotonically as the PDMS-glycol content was increased. The critical surface tension estimated by Zisman plots were 21-23 mN/m, the values are located between those of well-known hydrophobic polymers, poly(tetrafluoroethylene) and PDMS.

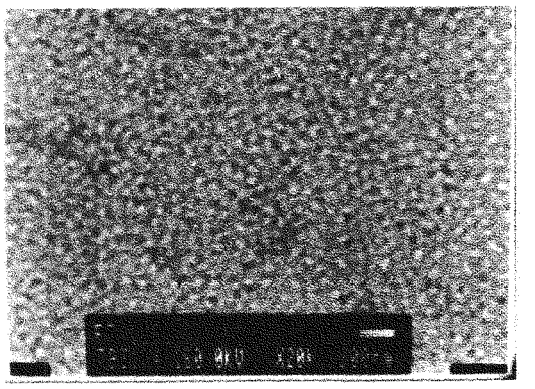


Fig. TEM of copolymer (**B**:**C**=1:7)