Release Layer Free Acrylate Resins
for Ultraviolet Nanoimprinting
Prepared by Adding Segregation Auxiliary Agents

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Ultraviolet nanoimprint lithography (UV-NIL) has received much attention because small line edge roughness of resist patterns useful in nano-device fabrication can be achieved. Formation of a release layer on a mold surface and addition of surfactants to UV-curable resins are proposed to improve release property of cured resin pattern from a mold. It is considered in general that a UV-curable resin to show a low surface free energy after curing is suitable to suppressing adhesion of cured resin to a mold surface. Therefore, UV-curable resins containing long-chain fluoroalkyl moieties have been intensively studied. In this report, we investigated surface segregation of long-chain fluoroalkyl moieties in UV-curable acrylate resins causing radical photopolymerization. It was found that heptadecafluoro-1,1,2,2-tetrahydrodecyl acrylate (17F-AC) in a glycerin 1,3-dimethacrylate (GDM) was effectively and cooperatively assembled at a cured resin surface by adding hexadecafluoro-1,1,9-trihydrononyl acrylate (16F-AC) which functioned as a segregation auxiliary agent. As a result, the diacrylate resin containing both 17F-AC and 16F-AC could be used as a release layer free UV-curable resin for UV nanoimprinting with a silica mold as shown in Fig. 1.

GDM was used as a base diacrylate monomer. Octafluoro-1,1,5-trihydropentyl acrylate (8F-AC), 16F-AC, and 17F-AC were used as additives. Irgacure 907 was used as a photoinitiator. Binary and ternary acrylate mixtures adding the photoinitiator were spincoated on silica plates modified with an adhesion monolayer, and the respective thin films were cured by exposure to UV light (0.1 W cm^{-2} @365 nm, 10 s). Figure 2 shows the surface free energy of the cure thin films calculated from contact angles for water and diiodemethane using Owens-Wendt equation, with results for the binary and ternary acrylate mixtures shown in Figs. 2(a) and 2(b), respectively. In the binary system, 16F-AC was miscible with GDM, while 17F-AC was not very miscible. A large amount of 16F-AC was necessary to form a low energy surface. Interestingly, a low energy surface could be prepared at a small fluorine atomic percentage (F at%) by mixing 17F-AC with 16F-AC in the ternary system. It was considered that 17F-AC cooperatively assembled with 16F-AC at the cured resin surface as illustrated in Fig. 3. The ternary acrylate mixture to show the lowest surface free energy after curing was available for UV nanoimprinting using a silica mold without a release layer.
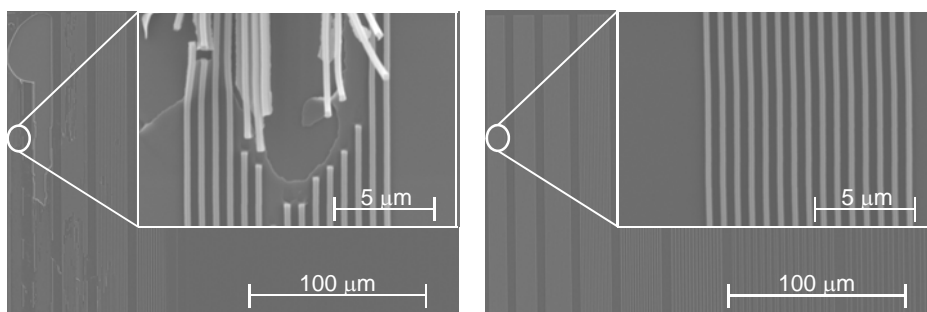
Fig. 1. SEM images of resin patterns prepared from (left) GDM and (right) ternary acrylate mixture (GDM, 17F-AC, and 16F-AC) by UV nanoimprinting under pentafluoropropane atmosphere using a silica mold without a release layer.
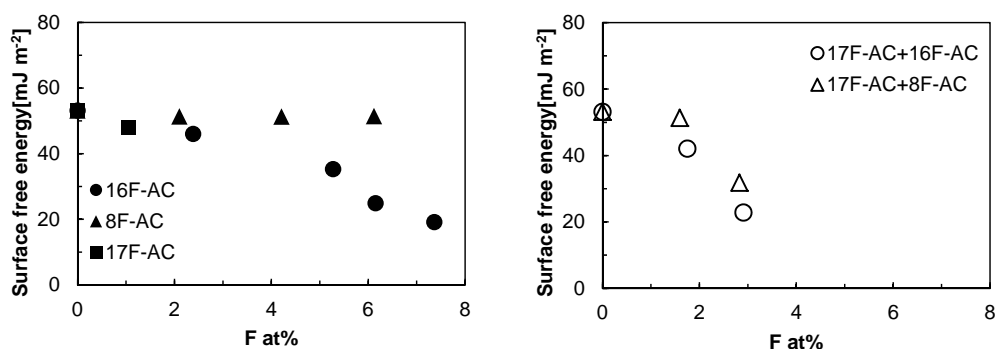

Fig. 2. Surface free energies of GDM cured films prepared from (a) binary acrylate mixtures with either 8F-AC, 16F-AC, or 17F-AC and (b) ternary acrylate mixtures with 17F-AC and either 8F-AC or 16F-AC. Curing was carried out by exposure to UV light for 10 s at an intensity of 0.1 W cm^2 monitored at 365 nm. The surface free energies were calculated from contact angles for water and diiodemethane using Owens-Wendt equation.
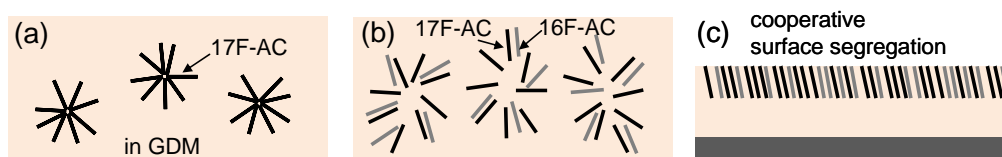

Fig. 3. Illustration of co-assembly of 17F-AC and 16F-AC at a cured resin surface. (a) 17F-AC is hardly miscible with GDM in binary system. (b) 16F-AC improves solubility of 17F-AC in GDM, and (C) 17F-AC and 16F-AC co-assembled at a resin surface in ternary system. 16F-AC functions as a segregation auxiliary agent for 17F-AC, which improves solubility of 17F-AC in GDM and assists surface segregation of 17F-AC by co-assembly.