

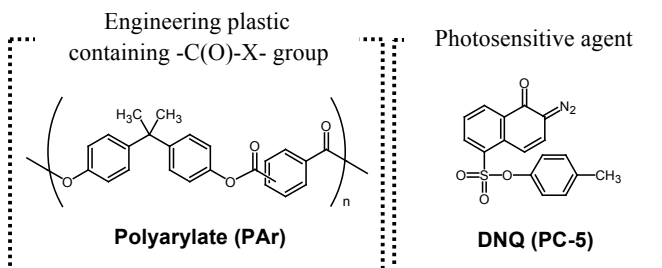
Improvement in properties of photosensitive polyarylates based on positive-tone reaction development patterning

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Introduction

Photosensitive polymers are defined as polymers whose solubility into developer is changed by photo-irradiation, and they are important materials for various areas such as fabrication of micropatterns in electronic industry. Our group has developed a novel pattern-forming method, "Reaction Development Patterning (RDP)", which gives positive-tone patterns by photo-irradiation to

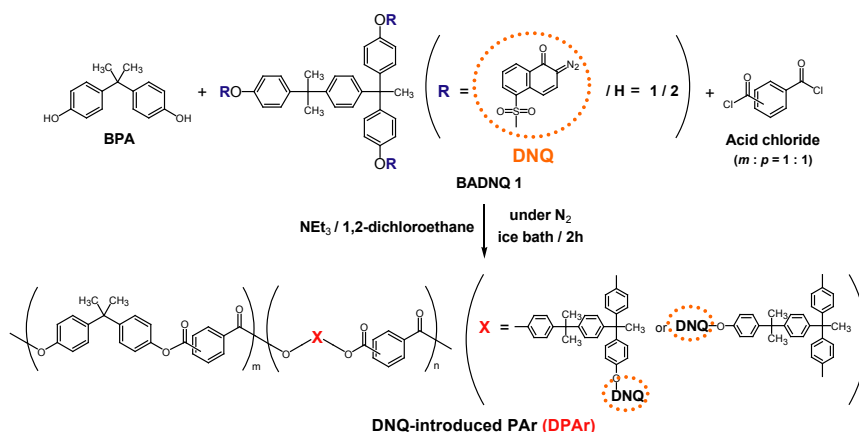


Scheme 1 An example of photosensitive polymer based on conventional RDP

films of engineering plastics with carboxylic-acid-derivative groups (*e.g.* polyarylate (PAR)) containing photosensitive agents (diazonaphthoquinones (DNQs)) (Scheme 1) and the following development with solutions containing ethanolamine (EA)¹. Pattern formation in RDP is based on scission of -C(O)-X- groups in a polymer by nucleophilic EA during development and photo-reaction of DNQ to acid promotes selective permeation of a developer to irradiated areas. While this method can easily add photosensitivity to various engineering plastics, properties of the prepared patterns are decreased in comparison with the original polymers because of addition of low-molecular-weight photosensitive agents. Therefore, in this study, we developed RDP-based photosensitive PARs not containing low-molecular-weight photosensitive agents but using PARs having DNQ groups in their chains.

Results and Discussion

DNQ-introduced PARs (DPArs) were synthesized as shown in Scheme 2, and their molecular weights and contents of DNQ were shown in Table 1. After film formation of the obtained DPArs, RDP was applied to the films, that is, the films were irradiated by ultra-high pressure mercury lamp



Scheme 2 Synthesis of DNQ-introduced PAR (DPAr)

through a photomask and then developed by EA / NMP / H₂O solution. As a result, all DPAr systems afforded fine positive-tone patterns (Table 1, Fig. 1(a)). Increase in DNQ content in DPAr and decrease in molecular weight realized shorter development time and higher resolution, while attempts to prepare DPArs having both large DNQ content and high molecular weight were unsuccessful.

Therefore, we then utilized DPArs as photosensitive agents for RDP by mixing DPArs and PAR. As a result, fine positive-tone patterns were afforded in shorter development time and higher resolution than conventional system using low-molecular-weight photosensitive agent (Table 2, Fig. 1(b)). Decrease in development time would be because introduction of BADNQ1 units into polymer chains promoted developer permeation and/or reaction between ester groups and EA.

Furthermore, we investigated properties of the prepared patterns. Because reactive diazo group in DNQs remained in formed patterns may have adverse influences on properties of the patterns, the obtained patterns were heat-treated at 210°C for an hour. As a result, the patterns were maintained their shape even after the heating (Fig. 1(c)). Results of dynamic mechanical analysis (DMA)

measurements of the heat-treated PAr films were shown in Fig. 2, and it was revealed that PAr / DPAr system had significantly better mechanical

property than PAr / low-molecular-weight DNQ (PC-5) system. In addition, PAr / DPAr film showed higher storage modulus than PAr itself, probably because of partial cross-linking during decomposition of the diazo groups.

Conclusions

Application of RDP to DPAr as polyarylates having photosensitive group in the structure were found to afford fine positive-tone patterns without addition of low-molecular-weight photosensitive agents. Moreover, utilization of DPAr as high-molecular-weight photosensitive agents for RDP-based photosensitive PAr systems resulted in successful positive-tone pattern formation in shorter development time and higher resolution than PAr / low-molecular-weight DNQ system. In addition, the patterns produced by this method showed better properties than conventional system using low-molecular-weight photosensitive agent.

Reference

1) T. Fukushima, T. Oyama et al, *J. Microlith. Microfab. Microsyst.*, **3**, 159-167 (2004).

Table 1 Results of pattern formation of DPAr films¹⁾

Entry	DNQ content [wt%]	M _n × 10 ⁴	PDI	Development time [min'sec]	Film thickness ^{2),3)} [μm]	Dissolution rate [nm/s]		Residual ³⁾ [-]	Resolution ⁴⁾ [μm]
						Exposed	Unexposed		
1	13	2.1	2.8	15'44	7.0 → 5.8	7.4	1.3	0.83	25
2	12	1.2	2.3	13'05	7.0 → 6.7	8.9	0.38	0.90	15
3	29	1.3	4.8	10'36	11.2 → 10.8	18	0.63	0.96	10
4	29	0.95	5.2	4'50	6.7 → 6.3	23	1.4	0.94	10
5	29	0.98	5.9	2'32	6.2 → 5.9	41	2.0	0.95	10

1) Exposure dose : 1000mJ/cm², Developer : EA / NMP / H₂O = 4 / 1 / 1 (w / w / w),

Development condition : 40-45°C / ultrasonication

2) By contact-type thicknessmeter 3) At unexposed areas 4) Confirmed by SEM

Table 2 Results of pattern formation of photosensitive PAr films¹⁾

Entry	Photosensitive agent (M _n × 10 ⁴)	DNQ content [wt%]	Development time [min'sec]	Film thickness ^{2),3)} [μm]	Dissolution rate [nm/s]		Residual ³⁾ [-]	Resolution ⁴⁾ [μm]
					Exposed	Unexposed		
1	DPAr (1.3)	20	8'06	10.6 → 10.1	22	1.0	0.95	10
2	DPAr (0.95)	20	12'35	10.0 → 9.6	13	0.53	0.96	10
3	DPAr (0.98)	20	9'38	8.9 → 8.8	15	0.17	0.99	10
4	DPAr (0.98)	13	22'42	8.7 → 7.9	6.4	0.59	0.91	10
5 ^{a)}	PC-5	13	45'32	9.6 → 6.8	3.5	1.0	0.71	30

1) Exposure dose : 1000mJ/cm², Developer : EA / NMP / H₂O = 4 / 1 / 1 (w / w / w),

Development condition : 40-45°C / ultrasonication

2) By contact-type thicknessmeter 3) At unexposed areas 4) Confirmed by SEM

a) Conventional system using low-molecular-weight photosensitive agent

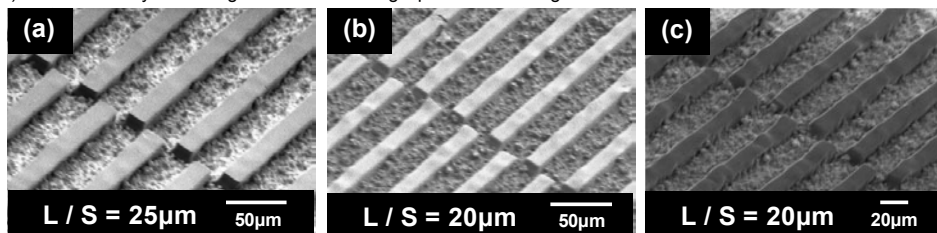


Fig. 1 SEM images of the prepared patterns

(a) Entry 3 in Table 1, (b) Entry 2 in Table 2, (c) Entry 2 in Table 2 after heat treatment

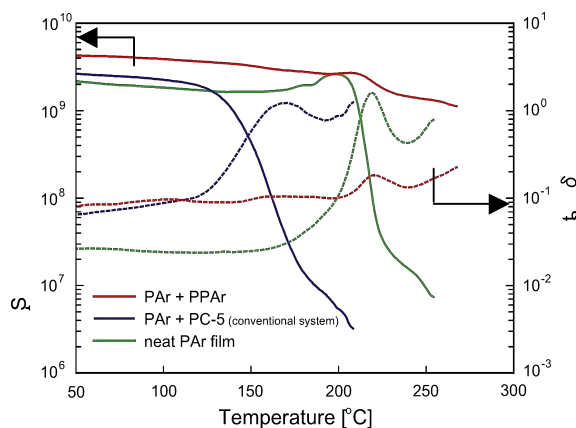


Fig. 2 DMA charts of heat-treated PAr films (Heating rate : 5°C/min, Frequency : 1Hz, under air)