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FOCUS REVIEW

Photosensitive engineering plastics based on reaction development patterning

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Abstract

Photosensitive engineering plastics as typified by photosensitive polyimides are mainly used in the electronics industry to form fine patterns for uses in which they will not be removed for a long time. However, to impart photosensitivity, it is necessary to introduce a functional group into a polymer or to use a precursor polymer, which hinders further applications of these polymers. We have developed reaction development patterning (RDP) as a method of forming a fine pattern by promoting the reaction between carboxylic acid derivatives in a polymer chain and nucleophiles in a developer selectively at the exposed or unexposed area. Since engineering plastics such as polyimide and polycarbonate inherently have carboxylic acid derivative groups in their main chain, RDP can easily impart photosensitivity to a wide range of polymers, including commercially available engineering plastics. By using RDP, it is possible to form both positive- and negative-tone patterns from the same polymer. In this review, I will describe recent developments in the study of photosensitive engineering plastics by focusing on RDP.

Introduction

Photosensitive polymers enable mass production of fine patterns by photoirradiation and development process and provide selective processing only at a target surface and facile preparation of complicated shapes. On the basis of such characteristics, photosensitive polymers are widely used in electric and electronic applications, such as a photoresist for forming an ultrafine pattern of an integrated circuit (IC), an interlayer dielectric film of a multilayer wiring board, and a buffer coat layer between an IC chip and an encapsulating resin [1–8]. They are also utilized for the production of various finely patterned components, including color filters of liquid crystal displays, optical waveguides, printing plates, and three-dimensional objects such as a micro-electro-mechanical system [9–11]. The properties required for photosensitive polymers are different in each of these applications, and photosensitive polymers suitable for each application have been in demand. For example, a photoresist used for forming an ultrafine pattern of an IC requires very high resolution (several tens of nm or less) and etching resistance. However, since the photosensitive polymer itself is ultimately removed, its long-term heat and mechanical resistance are not important. On the other hand, the resolution required for photosensitive polymers used as a buffer coat layer and as an interlayer dielectric film is lower than that required for a photoresist and is generally up to several μm. However, since the fine pattern formed is used without being removed over a long duration, high thermal and mechanical stability and electrical insulation properties are strongly required for photosensitive polymers.

Photosensitive polyimides are well known as photosensitive polymers used for applications that require long-term durability [3, 4, 6]. They enable the formation of fine patterns of polyimides, which are typical super engineering plastics. Both negatively and positively working photosensitive polyimides have been developed, in which the exposed part becomes insoluble and soluble, respectively. The design of conventional photosensitive polyimides is roughly divided into “impartment of photosensitivity by chemical modification of molecular structure of a polyimide

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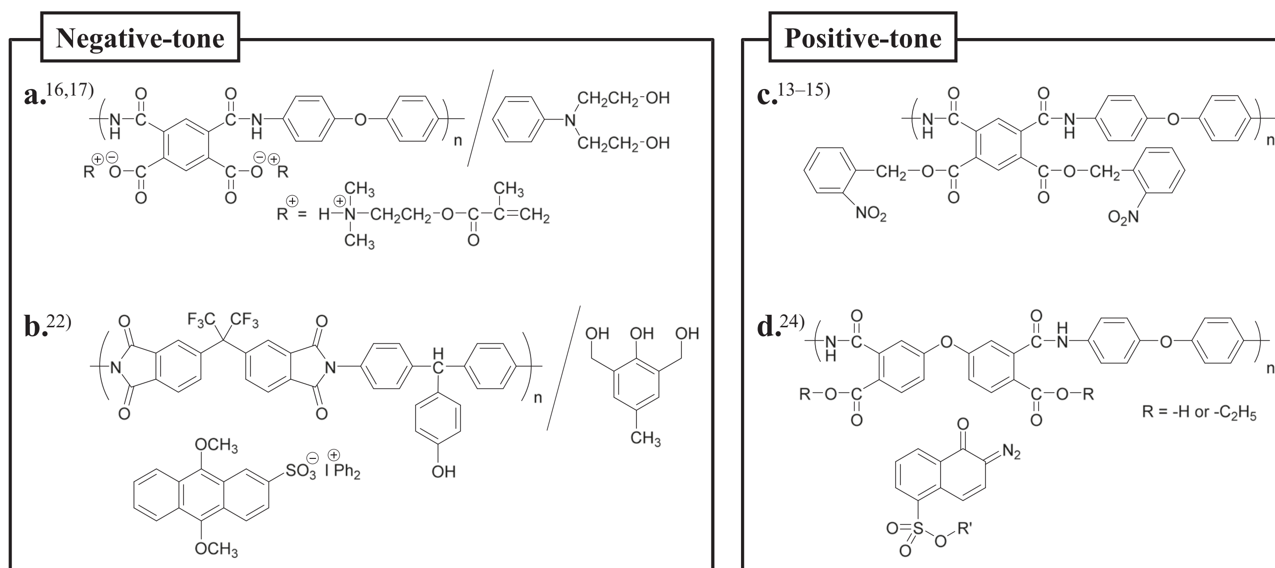

Fig. 1 Examples of conventional photosensitive polyimides

or poly(amic acid) as a polyimide precursor [12–15]" and "addition of low-molecular-weight additives (sensitizer, photoacid generator, photo-radical generator, etc.) to a chemically modified polyimide or poly(amic acid) [16–24]" (Fig. 1). However, chemical modification of a polyimide or poly(amic acid) results in complicated polymer synthesis and increased synthetic cost. Chemical modification also often reduces the excellent inherent physical properties of polyimide. Photosensitive varnishes using poly(amic acid) have poor storage stability, and fine patterns prepared from photosensitive poly(amic acid)s require conversion to polyimide by heating at >300 °C. On the other hand, imparting photosensitivity to engineering plastics other than polyimides is expected to broaden the scope of applications of photosensitive engineering plastics to fields in which conventional photosensitive polyimides could not be used due to problems such as their high costs. However, except for photosensitive poly(benzoxazole)s [3, 6, 25, 26], which, as with polyimides, require the use of precursors, few studies have been reported on imparting photosensitivity to other engineering plastics [3, 27]. Regarding the mechanism to obtain a difference in solubility between the exposed and unexposed areas, the previously reported photosensitive polyimides and poly(benzoxazole)s have utilized reactions during photoirradiation, i.e., acid generation or polymerization, as the key reactions, and the development process of conventional systems has only played a role in dissolving the easily soluble area.

In these circumstances, we have developed reaction development patterning (RDP), which is a fine-pattern formation method widely applicable to non-chemically modified engineering plastics containing carboxylic acid derivative group in their main chain, such as polyimides, polyesters, and polycarbonates. RDP is a technique utilizing the solubility change of a polymer during the development process induced by a nucleophilic acyl substitution reaction between carboxylic acid derivative groups in the polymer and nucleophiles (amine, OH^-, etc.) in a developer. By selectively causing this change in solubility at the exposed or unexposed areas, formation of both positive- and negative-tone fine patterns is realized. To the best of our knowledge, photosensitive engineering plastics utilizing polymer reactions during development as the key reaction have not been reported except for the pioneering examples using polyisoimide [28, 29]. Therefore, RDP can be regarded as a novel and useful method that can readily impart photosensitivity to a wide range of polymers, including commercially available engineering plastics. In this review, I will focus on the pattern formation mechanism and applicable range of the photosensitive engineering plastics based on RDP.

Positive-tone RDP

Photosensitive engineering plastic films used for positive-tone RDP are typically prepared by dissolving an engineering plastic with carboxylic acid derivative groups, including commercially available polyimides, polycarbonates and polyarylates (Fig. 2), and a diazonaphthoquinone (DNQ, Fig. 2) as a photosensitive agent in a cosolvent such as *N*-methylpyrrolidone (NMP) and spin-coating the solution. The obtained film is prebaked and then exposed to ultraviolet (UV) light from an ultrahigh pressure mercury lamp through a photomask. After the exposure,

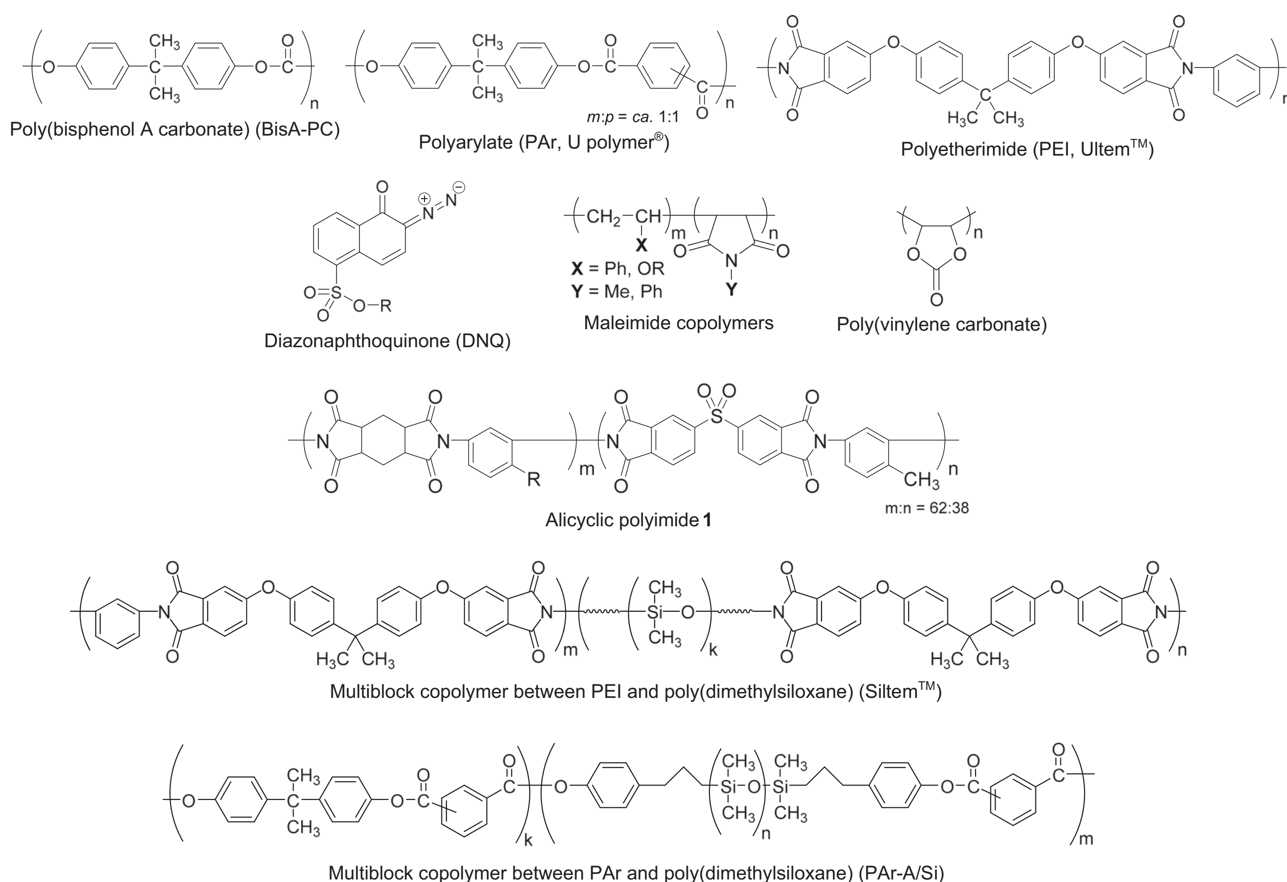

Fig. 2 Structures of the polymers and photosensitive agents appearing in this focus review

development is carried out using a hydrophilic developing solution containing a nucleophile such as ethanolamine to give a fine positive-tone pattern in which only the exposed area is dissolved [30–35]. Figure 3a, b shows scanning electron microscope (SEM) photographs of fine patterns formed by applying positive-tone RDP to commercially available polyetherimide (PEI, Ultem^{TM}) [34] and polycarbonate (BisA-PC) [31]. Formation of clear line and space (L/S) patterns with a resolution of 10 µm was confirmed in both the photosensitive engineering plastics tested. The sensitivities of these photosensitive engineering plastics, i.e., the exposure doses at which the ratio of the residual films becomes zero, were 2000 mJ/cm^2 for the photosensitive PEI and 1000 mJ/cm^2 for photosensitive BisA-PC.

Gel permeation chromatography (GPC) measurement of the exposed areas dissolved in the developer revealed that the molecular weight of the engineering plastics was lowered. The model reaction in a homogeneous system in which ethanolamine and engineering plastics were dissolved in a cosolvent also resulted in a decrease in the molecular weight of the engineering plastics. Furthermore, in the attenuated total reflection infrared spectra of the surfaces of a DNQ-containing PEI film whose development was stopped before complete dissolution of the exposed area, a decrease in the absorption derived from the imide C = O group and an increase in the absorption derived from the amide N–H group were observed only at the exposed area. From these results, it is considered that the pattern-forming mechanism of positive-tone RDP is as shown in Fig. 4. In the exposed area, (i) indenecarboxylic acid is formed from DNQ upon exposure; (ii) the acid then reacts with the amine in the developer to form a salt; (iii) the salt increases the hydrophilicity of the exposed area and improves the permeation of the developer; (iv) the nucleophilic acyl substitution reaction between the amine in the developer that had permeated into the exposed area and the carboxylic acid derivative groups in the engineering plastic cleaves the main chain of the engineering plastic; and (v) the exposed area with decreased molecular weight due to the main chain cleavage is dissolved in the developer. On the other hand, in the unexposed area, the acid generation during the first process does not occur, and therefore all subsequent processes do not occur, and dissolution of the polymer in the developer is suppressed.

Since RDP is a technique utilizing a nucleophilic acyl substitution reaction between a nucleophile in a developer and carboxylic acid derivative groups in a polymer, development time can be shortened by introducing electron-

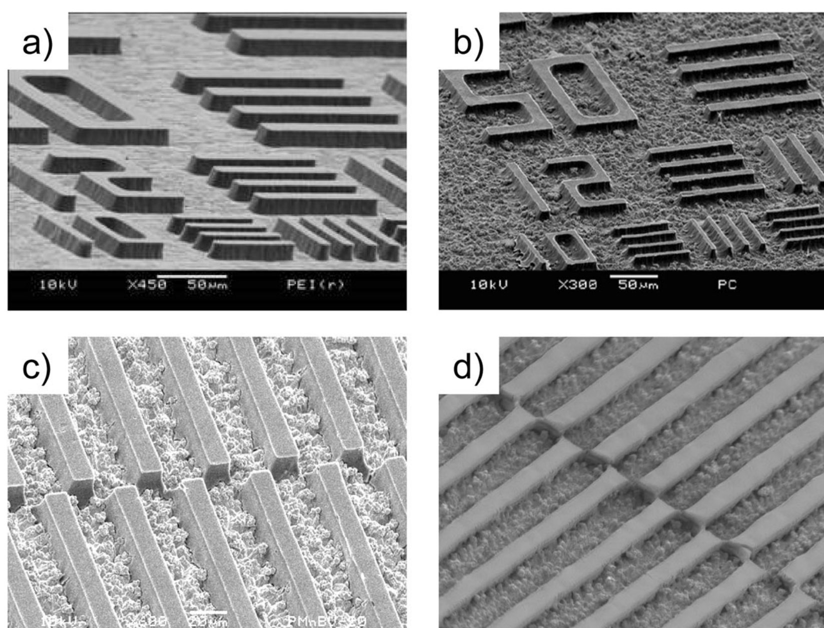

Fig. 3 SEM images of a fine positive-tone pattern obtained by applying RDP (DNQ: 30 wt% for each polymer). **a** PEI (Ultem^{TM}). Development: ethanolamine/NMP/water = 4:1:1 (by weight), 40–45 °C, ultrasonic treatment, 13 min. **b** BisA-PC. Development: ethanolamine/NMP/water = 1:1:1 (by weight), 40 °C, immersion, 7 min. **c** PM*n*BV. Development: $NH_2CH_2CH_2ONa$/ethanolamine/methanol (alkoxide/amine = 1:9 (molar ratio), (alkoxide + amine)/methanol = 3:1 (by weight)), 50 °C, immersion, 1 min 5 s. **d** P(VCA-VAc). Development: 5.0 wt% $NaOH_{aq.}$, 40 °C, immersion, 3 min

withdrawing groups into the polymer chain, as they improve the reactivity of the carbonyl group [36]. Positive-tone RDP is applicable not only to engineering plastics but also to a variety of polymers with carboxylic acid derivative groups in the main chain, such as poly(lactic acid) [37] and acid-anhydride-cured epoxy resin [38]. Furthermore, it is also possible to form a fine positive-tone pattern by applying RDP to polymers with carboxylic acid derivative groups at the side chains such as maleimide copolymers and poly(vinylene carbonate) (Fig. 2) [39–41]. For example, a fine pattern of poly(*n*-butyl vinyl ether-*co*-*N*-phenylmaleimide) (PM*n*BV) was prepared by positive-tone RDP using a developer containing an alkoxide ($NH_2CH_2CH_2ONa$) or tetramethylammonium hydroxide (TMAH) (Fig. 3c) [39, 40]. Application of positive-tone RDP to poly(vinylene carbonate-*co*-vinyl acetate) (P(VCA-VAc)) using a low-concentration aqueous sodium hydroxide solution as a developer achieved good fine-pattern formation by development for 3 to 7 min (Fig. 3d) [41]. The addition of a low-molecular-weight compound with a functional group such as a *t*-butyl ester, a 2-phenylethyl ester or an alkyl sulfate as an acid amplifier was found to improve the sensitivity of RDP-based photosensitive polyimides by a chemical amplification mechanism (Fig. 5) [42]. In chemically amplified RDP, an acid generated from the photosensitive agent by photoirradiation acts as a catalyst for deprotection of the acid amplifier. The deprotection of the acid amplifier is promoted by post-exposure baking, and the amount of acid is increased only at the exposed areas. The increased amount of acid then forms a salt with the nucleophile in the developer, and a positive-tone pattern is formed according to the RDP mechanism. In the chemical amplification mechanism, a large amount of acid is generated from a small number of photons, thereby improving the sensitivity of the system [43]. Therefore, the amount of photosensitive agent can be reduced by applying a chemical amplification mechanism.

A fine pattern formed by positive-tone RDP contains unreacted DNQ. However, as a result of measuring the coefficient of thermal expansion (CTE) of trifluoromethyl-group-containing polyimide (CF_3-PI) and DNQ-containing CF_3-PI, the influence of the presence or absence of DNQ on CTE was hardly observed [44]. In addition, the dielectric constant and dissipation factor measured after heating DNQ-containing CF_3-PI at 300 °C showed only a slight increase compared to the values of CF_3-PI itself [44].

Negative-tone RDP

The addition of low-molecular-weight components such as *N*-phenylmaleimide (PMI) to an RDP-based positive-tone photosensitive polyimide film composed of a polyimide and DNQ as a photosensitive agent achieves negative-tone fine-pattern formation [45]. A PEI film containing DNQ (PC-5, 15 wt% for PEI) and PMI (1 wt% for PEI) was irradiated with UV light from an ultrahigh pressure mercury lamp via a negative photomask with an exposure dose of 100 mJ/cm^2 and was immersed in an aqueous TMAH/alcohol developer (TMAH: 7.4 wt%) to form a fine negative-tone pattern. An SEM image of the obtained pattern and the sensitivity curve are shown in Fig. 6a, b, respectively. The sensitivity (D_{50}) of this system, i.e., the exposure dose at which the residual film becomes 50%, was 31 mJ/cm^2. This value is much higher than the sensitivity of positive-tone RDP, and it is

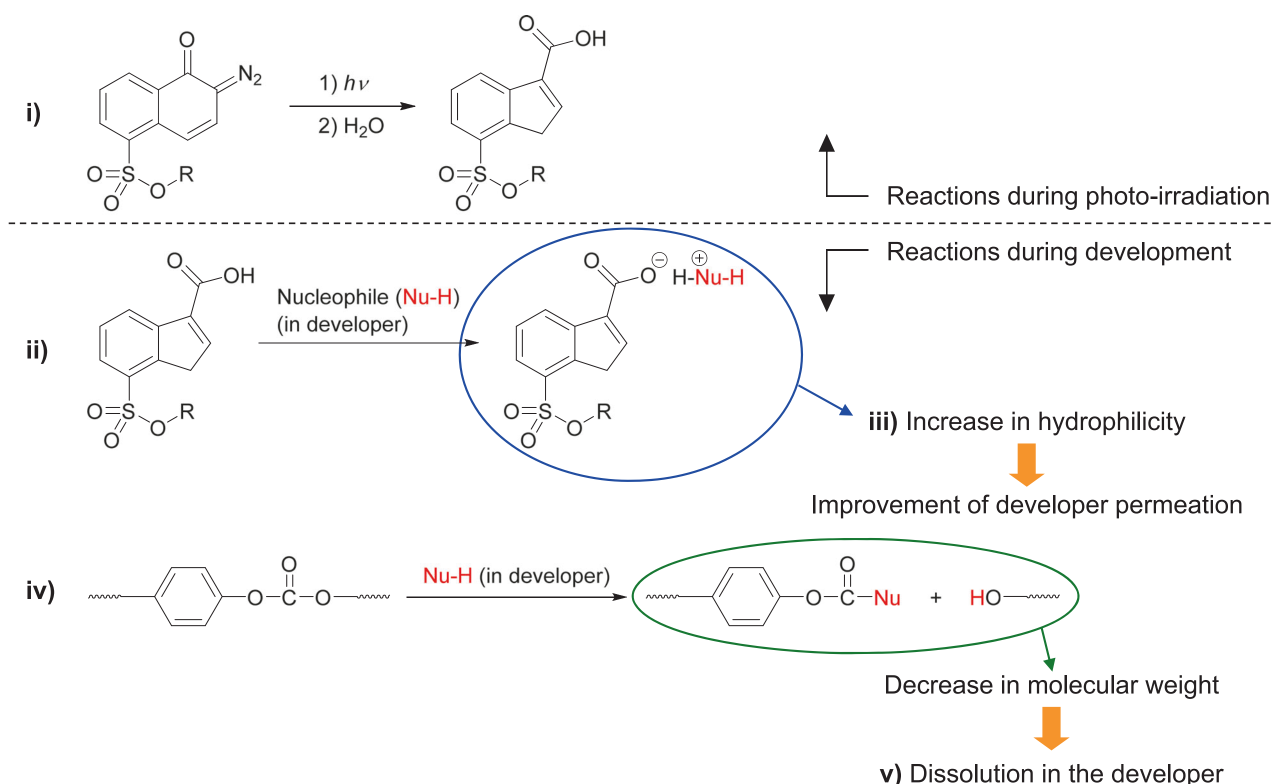

Fig. 4 Pattern-forming mechanism of positive-tone RDP

equal to or higher than that of the photosensitive polyimides currently being used industrially. In negative-tone RDP, the pattern could be formed by using a smaller amount of DNQ than that used in positive-tone RDP, in which the amount of DNQ added is usually 20–30 wt% of the polymer. Furthermore, it became clear that not only polyimides but also polycarbonates [46] and poly(lactic acid) [37, 47] could be used as the polymer components for negative-tone RDP.

GPC measurement of the components dissolved in the developer and ^{1}H-nuclear magnetic resonance spectroscopic measurement of the product of the model reaction between PEI and the developer in a flask showed that polyimide was dissolved in the developer as the salt of poly(amic acid) without lowering the molecular weight [45]. It was also revealed that *N*-substituted maleimides showed a high dissolution inhibiting effect on the exposed region during the development process when the solubility of the corresponding dimers formed by the [2 + 2] photocycloaddition of the maleimides was low [48–50]. PMI and *N*-cyclohexylmaleimide were representative examples of these maleimides, while the maleimides with short carbon chains such as *N*-methylmaleimide had a small dissolution inhibiting effect. Furthermore, in negative-tone RDP, it was indicated that TMAH in the developer was consumed by its reaction with indenecarboxylic acid generated from DNQ by photoirradiation and that this consumption made the reaction between engineering plastics and TMAH difficult to occur [51]. From these results, it was suggested that in negative-tone RDP, suppression of developer permeation by the dimerized PMI (**1b** in Fig. 7) and consumption of OH^- by the reaction of indenecarboxylic acid with TMAH (**2** in Fig. 7) inhibit the conversion from polyimide to poly(amic acid) at the exposed area (**3** in Fig. 7) to give a fine negative-tone pattern.

The negative-tone RDP of PEI is achieved only when developers consisting of an aqueous alkaline solution and organic solvents are used. However, if a fine pattern can be formed by development with a low-concentration alkaline aqueous solution as with the currently employed photosensitive polyimides, the usefulness of RDP is further enhanced. As shown in Fig. 7, in negative-tone RDP, the exposed area dissolves in the developer by the conversion from a polyimide to the corresponding poly(amic acid) during development. Therefore, a polyimide that can be applied to RDP using an aqueous alkaline solution as a developer must simultaneously satisfy the following two requirements: (i) the corresponding poly(amic acid) is soluble in aqueous alkaline solution, and (ii) the polyimide itself is soluble in a solvent for preparing the additive-containing film by spin-coating or application. To satisfy the first requirement, it is necessary to shorten the distance between amic acid groups in the polymer chain. On the

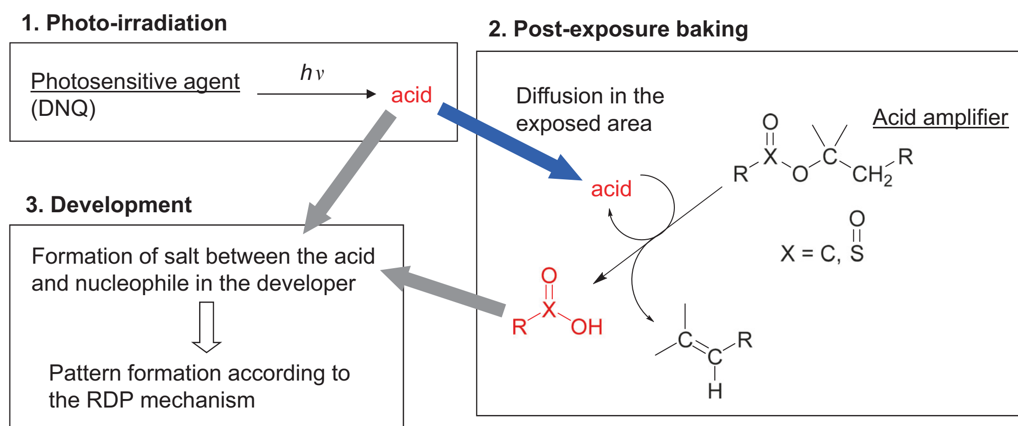

Fig. 5 Application of a chemical amplification mechanism using acid amplifiers to RDP

other hand, it is known that a polyimide with a short distance between imide groups has high rigidity and generally low solubility. Therefore, to satisfy both of the above two requirements, the molecular structure of the polyimide should be appropriately designed. As an example of a polyimide satisfying requirements (i) and (ii), we synthesized alicyclic polyimide **1** (Fig. 2) [52]. The film of the polyimide **1** containing DNQ (PC-5), PMI and 5-hydroxyisophthalic acid was exposed through a negative photomask and then developed with 2.5 wt% TMAH aqueous solution, which is an industrial-level low-concentration developer. As a result, a clear fine negative-tone pattern was formed with a development time of 6 min 24 s (Fig. 6c). The sensitivity curve of this system is shown in Fig. 6d. The sensitivity (D_{50}) was 50 mJ/cm^2 when a film with an initial thickness of 10 μm was used, and it became clear that RDP-based photosensitive polyimide **1** had a sensitivity equal to or higher than that of the photosensitive polyimides currently in practical use.

Application of RDP to hybrid polymers between engineering plastics and inorganic components

Organic–inorganic hybrid materials in which organic and inorganic components are dispersed at the nanometer or molecular scale and element-block polymers with an "element block" as a structural unit consisting of various groups of elements in a polymer chain can synergistically express properties and functions derived from their organic and inorganic components [53, 54], and a variety of materials that realize hybridization by covalent bonds, hydrogen bonds, π-π interactions, etc. have been reported.

It is expected that imparting photosensitivity to these hybrid materials and element-block polymers will enable facile formation of high-performance fine patterns, and various attempts have been made to date [8, 55, 56]. However, few studies on photosensitive hybrids using super engineering plastics such as polyimides have been reported, although they are expected to give fine patterns with excellent thermal and mechanical stability and low thermal expansion. In particular, to the best of our knowledge, photosensitive organic–inorganic hybrids using engineering plastics other than polyimides and polybenzoxazoles have not been reported. For the hybrids using polyimides and polybenzoxazoles, only systems with low versatility such as a long-time exposure system of a photosensitive polyimide utilizing the photocrosslinking of a benzophenone moiety in the main chain [57] and systems using poly(amic acid) and its derivatives [58–60] have been reported.

As described in the previous sections, RDP is a fine-patterning method utilizing the carboxylic acid derivative groups originally present in polyimides, polyesters, etc. and is therefore a highly versatile technique for imparting photosensitivity to such engineering plastics. Thus, it is expected that RDP can also readily impart photosensitivity to hybrid systems between polyimides or polyesters and inorganic components. To investigate the applicability of RDP to engineering plastic-inorganic hybrid systems, negative-tone RDP was applied to Siltem™ (Fig. 2), which is a multiblock copolymer between PEI and poly(dimethylsiloxane) [61]. A film of Siltem™ containing PMI and DNQ (PC-5) was prepared and exposed to UV light from an ultrahigh pressure mercury lamp through a photomask. Subsequently, when this film was developed with a developer composed of TMAH/water/NMP/methanol, the formation of a fine negative-tone pattern was confirmed (Fig. 8a).

Then, fine-pattern formation by applying positive-tone RDP to a multiblock copolymer between a polyarylate and poly(dimethylsiloxane) (PAr-A/Si, Fig. 2) was investigated [62]. A cyclopentanone solution containing PAr-A/Si (k:m = 11:1) and a photosensitive agent (DNQ) was spin-coated and then prebaked to give a dry film that did not contain any solvent. This film was exposed to UV light from an

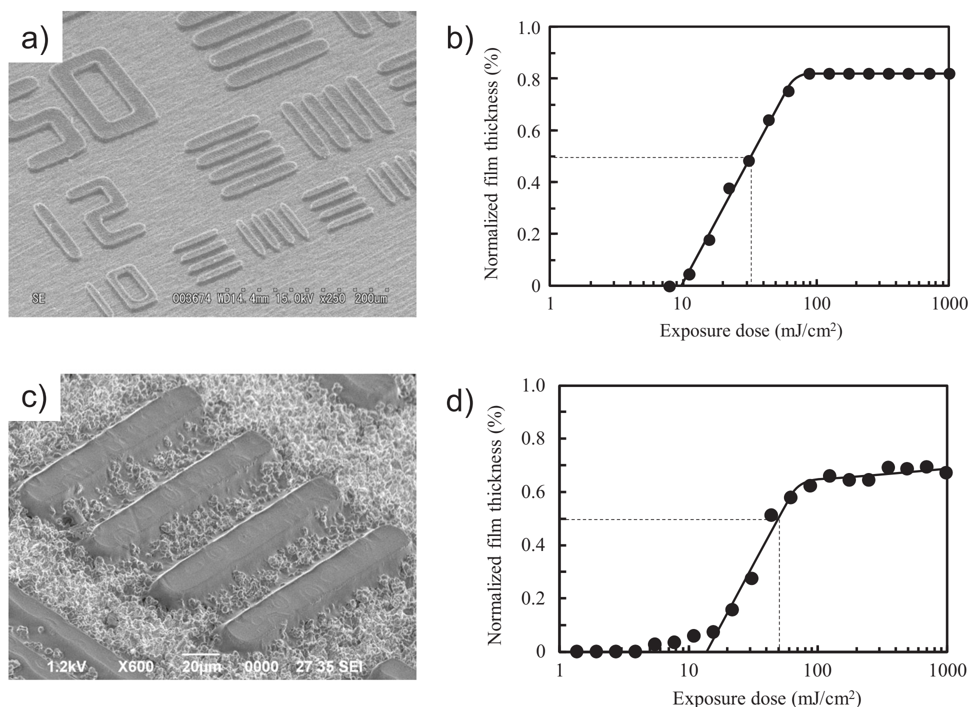

Fig. 6 SEM images of the fine pattern (**a**, **c**) and sensitivity curves (**b**, **d**) of negative-tone RDP. **a**, **b** Photosensitive PEI (Ultem^{TM}). Development: TMAH/water/PEG400/ethanol = 2:8:5:12 (by weight, PEG400 = poly(ethylene glycol) (M = 400)), 50 °C, immersion, 8 min 20 s. **c**, **d** Photosensitive alicyclic polyimide **1**. Development: 2.5 wt% $TMAH_{aq.}$, rt, immersion, 6 min 24 s

ultrahigh pressure mercury lamp through a photomask. Then, the film was immersed in a developer of ethanolamine/H_2O = 8:1 (w/w) under ultrasonic treatment, and as a result, a fine positive-tone pattern was obtained (Fig. 8b). This result indicates that introduction of a silicone unit into the main chain of PAr enables RDP from a dry film. In the conventional RDP process, it is important for successful pattern formation that a certain degree of solvent remains in the film after prebaking. In fact, when RDP was applied to photosensitive films of PAr without the silicone unit, fine patterns were not formed from the film in which the amount of residual solvent was decreased due to the severe prebaking conditions (Fig. 8c). Realizing fine-pattern formation from a dry film enables storage of RDP-based photosensitive polymers as films instead of solutions, which is expected to allow further expansion of the application range of RDP.

Introduction of the silicone unit into the PAr main chain also improved the sensitivity and development time. The sensitivity D_0 of PAr-A/Si (k:m = 11:1) was 189 mJ/cm^2, whereas that of PAr without the inorganic component was 600 mJ/cm^2. In addition, a good fine pattern was formed from the dry film of photosensitive PAr-A/Si after 2.5 min of development, while in the case of photosensitive PAr prebaked under severe conditions, the film thickness at the exposed area decreased only by 8% in the development for 15 min despite the presence of residual NMP used for spin-coating in the film.

Summary

In this review, we have described the impartment of photosensitivity based on RDP to various polymers, including engineering plastics as typified by polyimides. RDP is a novel technique for forming fine patterns using a nucleophilic acyl substitution reaction between carboxylic acid derivative groups originally present in the main chain of engineering plastics and nucleophiles in developers during the development process. In RDP, it is unnecessary to introduce acidic or polymerizable groups into engineering plastics, although these functional groups are indispensable for conventional photosensitive engineering plastics. Therefore, RDP has the advantages that commercially available engineering plastics can be used and that flexible molecular design is possible even when synthesis of the polymers for RDP is required. By using RDP, both fine positive- and negative-tone patterns can be formed, and various nucleophilic developers, such as amines, alkoxides, mixtures between aqueous alkaline solutions and organic solvents, and dilute aqueous alkaline solutions, can be used for RDP. In particular, photosensitive polyimides based on negative-tone RDP have excellent properties equal to or superior to those of currently industrialized photosensitive polyimides, such as high sensitivity, development with a dilute aqueous alkaline solution, good storage stability and formation of polyimide pattern without high temperature heating after development process. In addition, since negative-tone RDP achieves fine-pattern formation

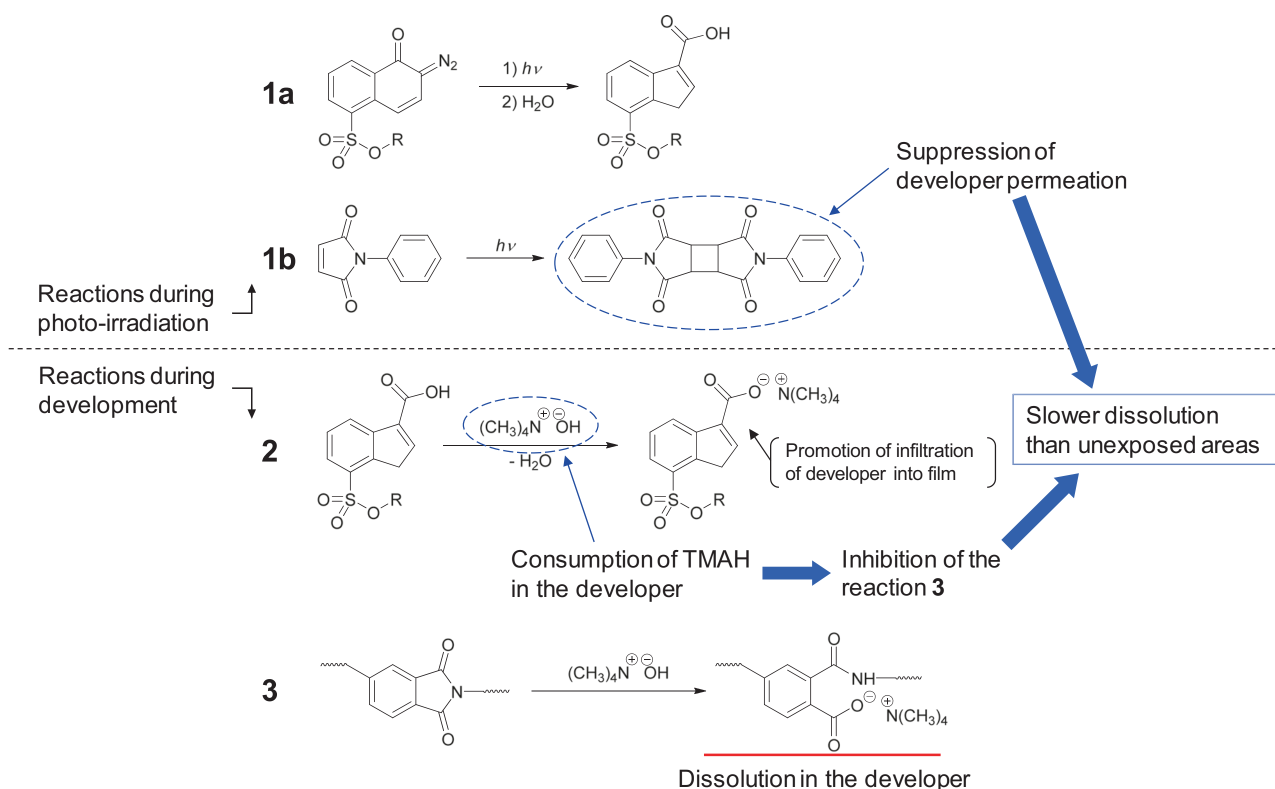

Fig. 7 Pattern-forming mechanism of negative-tone RDP

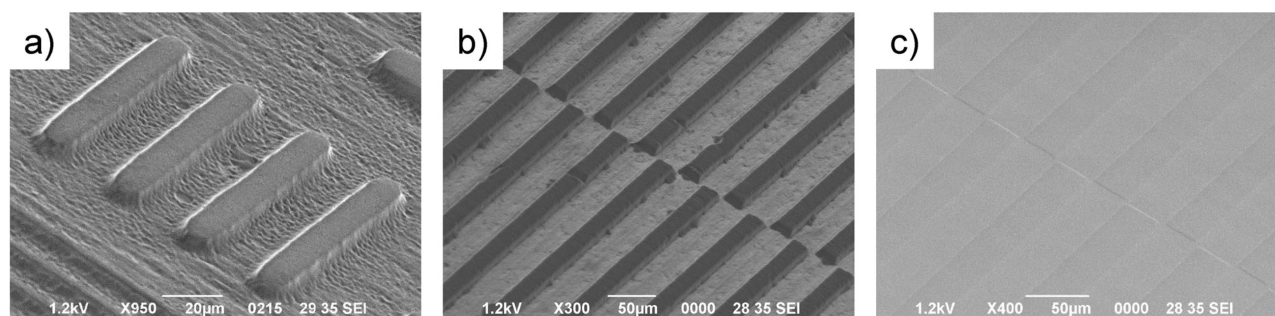

Fig. 8 SEM images of the fine pattern of hybrid polymers between engineering plastics and poly(dimethylsiloxane). **a** Negative-tone pattern of photosensitive Siltem^{TM}. Development: TMAH/water/NMP/methanol = 2:5:10:18 (by weight), 50 °C, ultrasonic treatment, 5 min 10 s. **b** Positive-tone pattern formed from photosensitive PAr-A/Si dry film: development: ethanolamine/water = 8:1 (by weight), 40 °C, ultrasonic treatment, 2 min 30 s. **c** Unsuccessful positive-tone pattern formation using the severely dried photosensitive PAr film. Development: ethanolamine/water = 8:1 (by weight), 40 °C, ultrasonic treatment, 15 min

without crosslinking the polymers, there is no reduction in resolution due to swelling of the pattern during development.

It was also revealed that RDP realizes facile fine-pattern formation from hybrid polymers between engineering plastics and inorganic components. In this review, we showed only the examples in which the engineering plastics and inorganic components were linked by covalent bonds. However, in a preliminary study, we also found that RDP could impart photosensitivity to a system in which an engineering plastic and a silica-based inorganic component are hybridized by non-covalent interaction [63]. Even when various element blocks are introduced into engineering plastics by methods other than those described in this review, it is believed that, in principle, fine patterns of these polymers can be formed by RDP as long as carboxylic acid derivative groups are present in the repeating units of the engineering plastics.

For the photosensitive polyimides currently used for electronic materials, a dilute aqueous alkaline solution (2.38 wt% TMAH aqueous solution) has been adopted as a developer. Thus, it is necessary to achieve short-time development using a dilute aqueous alkaline solution in order to put photosensitive polyimides based on RDP into practical use in this field. Although we have achieved negative-tone pattern formation of an alicyclic polyimide by RDP using 2.5 wt% TMAH aqueous solution as a developer (Fig. 6c, d), the development time and the residual thickness of the pattern to be formed should be further improved for practical use. In addition, the heat resistance of the alicyclic polyimide is usually slightly lower than that of fully aromatic polyimides. We will overcome the above-mentioned problems by optimizing the polyimide structure and development conditions and will realize photosensitive polyimides that can be commercialized in electronic material applications.

The RDP of commercially available engineering plastics requires an organic nucleophile and/or solvent as developer components, and this limitation on developers has narrowed the application range of RDP. Thus, we will continue to study the reduction in the amount of organic components in the developers for the RDP of commercial engineering plastics. We will also search for applications that allow the use of organic developers in order to apply the existing RDP of commercial engineering plastics as it is. Furthermore, we will work on further improvements in the performance of RDP-based photosensitive polymers, such as resolution, sensitivity and physical properties of the pattern to be formed, because photolithography processes using organic developers can be adopted even in applications in which an aqueous development process is currently used if their performances as photosensitive polymers are excellent [64].

In the future, we expect that photosensitive engineering plastics based on RDP will be put into practical use in various applications by optimizing the physical properties of the formed pattern according to the applications.

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Compliance with ethical standards

Conflict of interest The author declares that he has no conflict of interest.

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