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Dissolution Inhibitory Effect of a Urea Additive on a Carboxyl Polymer through a Supramolecular Structure

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ABSTRACT: The effect of the addition of carbonyl compounds such as amide, imide, urea, and ester derivatives on the dissolution rate of carboxyl-group-containing polymers in an alkaline solution was investigated. Urea derivatives lowered the dissolution rate of the polymer film more than the other carbonyl compounds did, and 1,3-diphenylurea inhibited the dissolution of the polymer film much more efficiently than other urea derivatives. Structural studies of the dissolution inhibition led to the proposal of a supramolecular structure, in which the urea functionality hydrogen bonded to two carboxyl groups of the polymer to form a hydrophilic domain surrounded by the hydrophobic substituents of the urea derivatives. The existence of this supramolecular structure is supported by the infrared spectra of the urea additives in the polymer films.

Introduction

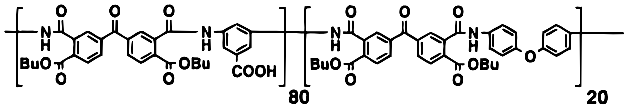
A dissolution inhibitory effect of photoactive compounds is an important characteristic, which improves the lithographic performance of photoresists. There have been many reports on novolac/diazonaphthoquinone (DNQ) resists wherein the dissolution inhibitory effect of DNQ plays an important role in enhancing both resolution and sensitivity.[1] However, there have been only a few reports concerning compounds that inhibit dissolution of the carboxyl polymer films in an alkali solution[2] though carboxylic polymers have been widely used for 193 nm photolithography[3] together with photosensitive polyimides.[4,5] Therefore, we have been interested in dissolution inhibitors of carboxyl polymers in an alkali solution as a way to improve lithographic performance.

In novolac/DNQ resists the hydrogen bonding between the carbonyl group of DNQ and several hydroxyl groups of the novolac resin led to a high inhibitory effect.[1] Thus, we expected that hydrogen bonding between additives and carboxyl polymers should bring about the dissolution inhibition of polymer films. Since it was reported that *N*-methylpyrolidinone (NMP) hydrogen bonded to the carboxyl group of a polyamic acid in the film state,[6] we focused on carbonyl additives that should interact with carboxyl groups in the polymers by hydrogen bonding. We employed polyamic acid butyl ester (PAE) as the carboxyl polymer. This PAE has a pendant carboxyl group (Scheme 1) and exhibits a moderate dissolution rate (1.0 μm/min) in the conventional alkaline developer, 0.262 N aqueous tetramethylammonium hydroxide (TMAH).

Results and Discussion

Dissolution Rates of PAE Films Containing Additives. We chose amides (sarcosine anhydride (**Am1**), 2,3-dimethoxy-*N*,*N*,*N*′,*N*′-tetramethylsuccinamide (**Am2**), *N*,*N*′-hexamethylenebis(acetamide) (**Am3**), *N*-benzylbenzamide (**Am4**)), imides (*N*-methylmaleimide (**Im1**), *N*-phenylmaleimide (**Im2**), benzimide (**Im3**), *N*-methylbenzimide (**Im4**), *N*-phenylbenzimide (**Im5**), *N*-methylsuccinimide (**Im6**), *N*-acetyl-ϵ-caprolactam (**Im7**)), esters (dibutyl phthalate (**Es1**)), 1,4-ditoluenesulfoxybenzene (**Su1**), sulfonamide (*N*-toluyltoluenesulfonamide (**Su2**), and 1,3-diphenylurea (**Ur1**) as an additive; their structures are depicted in Scheme 2. The dissolution rates of the polymer films containing additives are listed in Table 1. Most of the polymer films containing amides, imides, and esters had greater dissolution rates than that of the polymer (1.0 μm/min). Among these additives, **Im1**, **Im6**, **Am4**, and **Su1** lowered the dissolution rate of the polymer to 0.62, 0.60, 0.43, and 0.35 μm/min, respectively. However, even the film with **Am4**, which showed the largest reduction in the dissolution rate (0.35 μm/min), had one-third the dissolution rate of the polymer. In contrast, **Ur1** decreases the dissolution rate of the polymer by 1/13 (0.080 μm/min); this dissolution rate was considerably lower than those of the films with other additives.

Scheme 1



In the Introduction, we describe particular interactions such as hydrogen bonding between additives and polymers that would be essential to the dissolution inhibitory effect of the additives. However, we should take in account the hydrophobicity of the additives in estimating the dissolution inhibitory effect since the dissolution rate of the film gradually decreases as the hydrophobicity of the additives increases. We estimated the hydrophobicity of the additives using the logarithmic partition coefficient of 1-octanol:water (log *P*),[7] which is widely used as a hydrophobic parameter in the field of the quantitative structure−activity relationship (QSAR) for predicting transport properties, pharmacological activity, environmental activity, and toxic effects of organic molecules.[7,8] The log *P* of all the additives

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Scheme 2

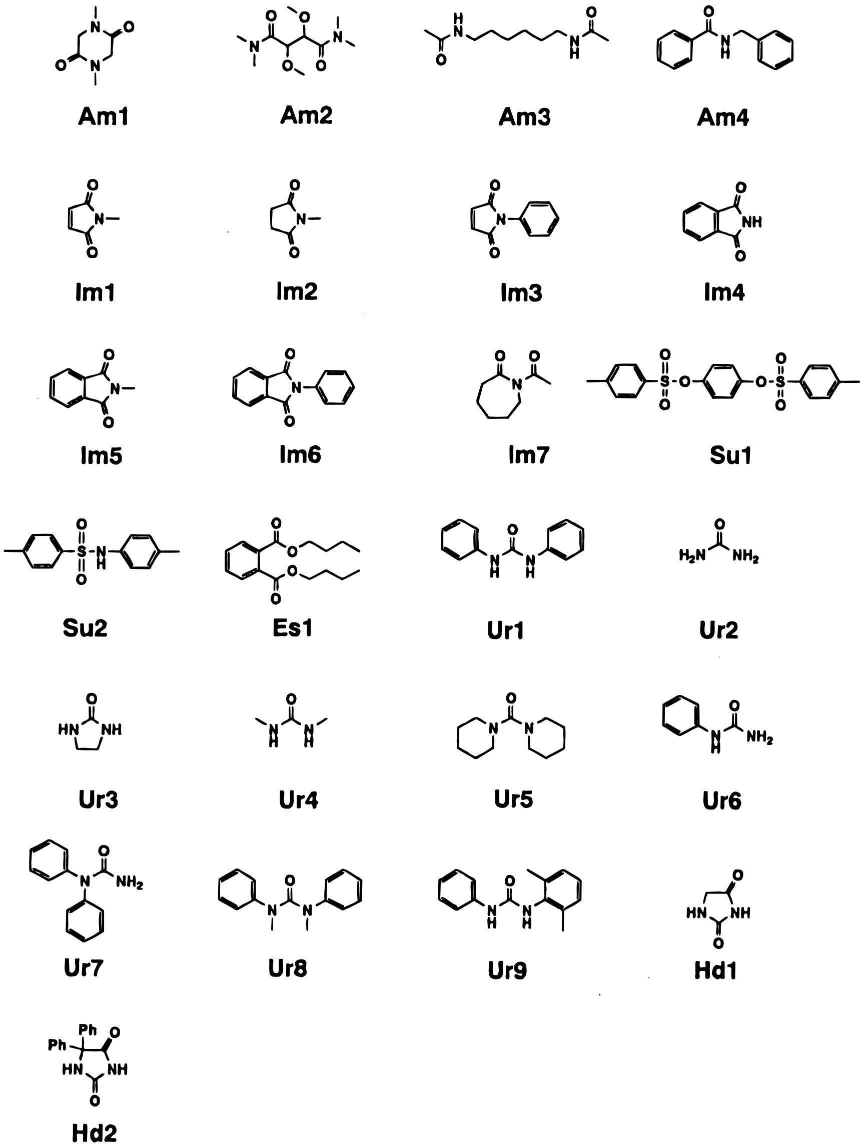


Table 1. Physical Parameters of Carbonyl Additives and the Dissolution Rates of the PAE Films Containing the Carbonyl Additives

	additives	vol (Å^3)	log *P*	DR (μm/min)
film				1.0
amide	**Am1**	130	−0.76	5.6
	Am2	223	−0.53	5.4
	Am3	206	0.21	2.5
	Am4	207	1.7	0.35
imide	**Im1**	96.0	0.063	0.62
	Im2	101	−0.36	1.9
	Im3	153	0.53	1.3
	Im4	123	0.14	1.5
	Im5	141	0.39	1.7
	Im6	197	0.85	0.60
	Im7	150	0.62	1.4
sulfone	**Su1**	335	2.17	0.43
	Su2	235	0.755	3.1
ester	**Es1**	267	2.84	1.5
urea	**Ur1**	201	1.12	0.080

are calculated using atomic parameters derived by Ghose et al. and listed in Table 1.[9]

The dissolution rates of the polymer films containing the additives are plotted versus log *P* in Figure 1. As expected, the dissolution rates of the films with amides, imides, and esters decreased with increasing log *P* with a correlation coefficient (*r*) of 0.75 (see the straight line in Figure 1).[10,11] Therefore, the dissolution rates were decreased only by increasing the hydrophobicity of the additives with no influence by specific interactions between the additives and the polymer. It should be noted that the dissolution rate of the film with **Ur1** is much lower than the dissolution rates of the films with amides, imides, and esters even though **Ur1** is similar in hydrophobicity (log $P = 1.12$) to **Am4**, **Su1**, and **Es1**. The exceptionally low dissolution rate of the film with **Ur1** compared with the films with other additives strongly indicates that **Ur1** interacts with the polymer, probably by hydrogen bonding.

Since only 1,3-diphenylurea (**Ur1**) exhibited a substantial dissolution inhibition of the polymer film, we examined other urea derivatives containing a variety of substituents (Figure 2). Among nonaromatic ureas, urea (**Ur2**), imidazolidone (**Ur3**), and 1,3-dimethylurea (**Ur4**) slightly suppressed the dissolution rates of the polymer (0.77, 0.65, and 0.71 μm/min). These dissolution rates were lower than those of nonaromatic amides and imides, which possess similar hydrophobicities, ranging from −0.8 to +0.7 in log *P*. This difference indicated that the nonaromatic ureas have some inhibitory effect on

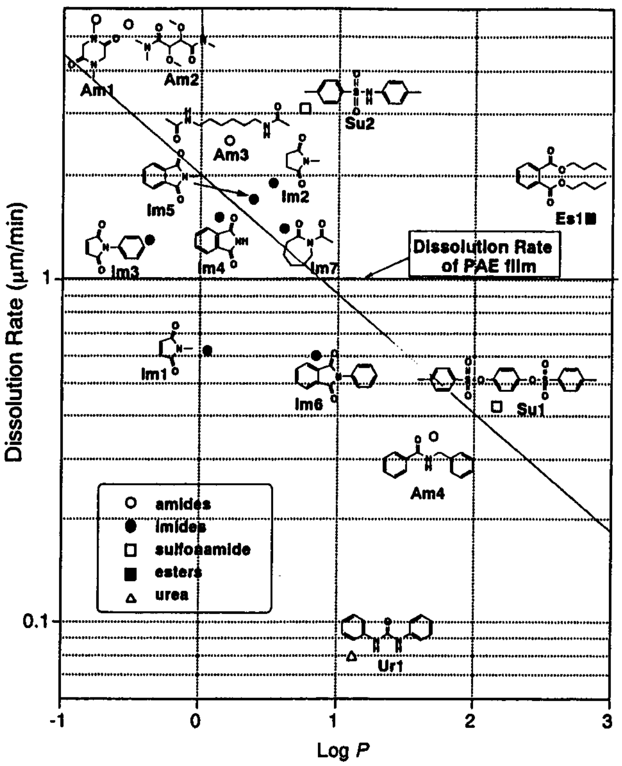


Figure 1. Dissolution rates of PAE films containing carbonyl additives versus a logarithmic partition coefficient of 1-octanol: water (log P) of the additives.

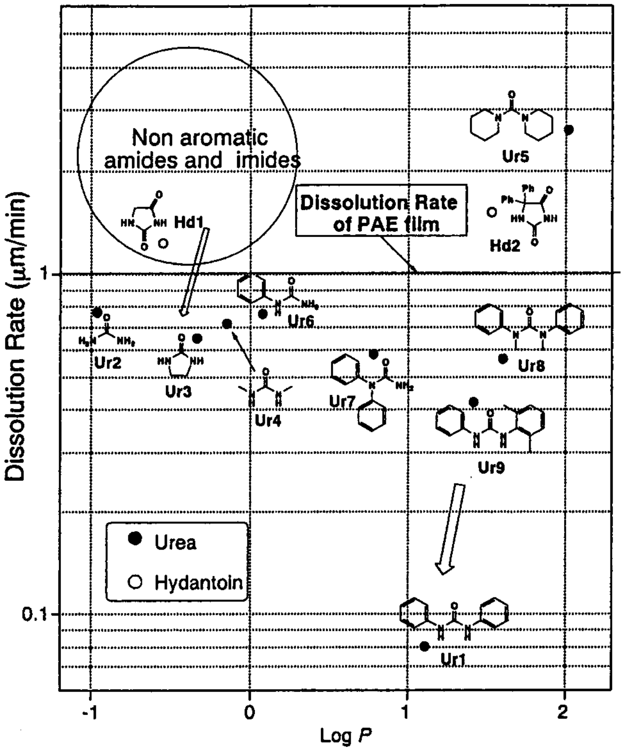


Figure 2. Dissolution rates of PAE films containing ureas versus a logarithmic partition coefficient of 1-octanol:water (log P) of the urea derivatives.

Table 2. Physical Parameters of Urea Derivatives and the Dissolution Rates of the PAE Films Containing the Urea Derivatives

	additives	vol (Å^3)	log P	DR (μm/min)
film				1.0
urea	**Ur1**	202	1.1	0.080
	Ur2	52.0	−0.96	0.77
	Ur3	77.3	−0.33	0.65
	Ur4	87.6	−0.14	0.71
	Ur5	201	2.0	2.6
	Ur6	126	0.078	0.76
	Ur7	202	0.79	0.58
	Ur8	226	1.6	0.56
	Ur9	235	1.4	0.42
hydantoin	**Hd1**	78.3	−0.54	1.2
	Hd2	225	1.5	1.5

the polymer dissolution compared with other nonaromatic carbonyl additives. Bis(pentamethylene)urea (**Ur5**) promoted the dissolution rate (2.6 μm/min) despite its large log P, probably due to the lack of hydrogen atoms, which are necessary for hydrogen bonding with carboxyl groups of the polymer, bonded to nitrogen atoms. Two hydantoin derivatives, hydantoin (**Hd1**) and 5,5-diphenylhydantoin (**Hd2**), showed no dissolution inhibition (1.2 and 1.5 μm/min) probably due to the acidity of the imide proton of the hydantoins (pK_a = 9.15)[12] (see Table 2).

Aromatic ureas, phenylurea (**Ur6**), 1,1-diphenylurea (**Ur7**), 1,3-dimethyl-1,3-diphenylurea (**Ur8**), and 1-phenyl-3-xylylurea (**Ur9**) gave dissolution rates, ranging from 0.5 to 0.8 μm/min, which were located in the same region as the other additives shown in Figure 1. It should be noted that only **Ur1**, which has a similar structure to the other aromatic ureas, has a significant inhibitory effect. To elucidate the role of the substituents of the urea additives in the dissolution inhibition, we compared the structures of the aromatic ureas with that of **Ur1**: replacing one phenyl group at one nitrogen atom of **Ur1** with one hydrogen atom leads to **Ur6**; transferring one phenyl group at one nitrogen to another nitrogen atom of **Ur1** leads to **Ur7**; replacing one hydrogen atom at each nitrogen atom of **Ur1** with a methyl group leads to **Ur8**. Since these replacements caused 7−10-fold decreases in the inhibitory effect of the polymer dissolution, we can conclude that both hydrogen atoms and phenyl groups at both nitrogen atoms of the urea additives would be the minimum requirement for the dissolution inhibitory effect.

Supramolecular Structure Model for Dissolution Inhibition. From the structural studies we propose the supramolecular structure model for the dissolution inhibitory effect as shown in Figure 3; a urea functionality leads to hydrogen bonding with two carboxyl groups of the polymer to form a hydrophilic domain, which is surrounded by the hydrophobic substituents of the urea derivatives. The separation of hydrophobic domains from hydrophilic domains results in the large dissolution inhibition of the carboxyl polymer film, which have been well elucidated by Reiser et al. as the "percolation model"[1d,e] and by Willson et al. as the "probabilistic model".[1g−i] The supramolecular structure model looks similar to the "octopus pot" model reported by Tachibana et al.[1a,b] for novolac/diazonaphthoquinone-based photoresists. However, this supramolecular model is differentiated from the previous models by possessing the strict structure dictated by exact hydrogen-bonding pairs between the urea additives and the polymers. The supramolecular model is also consistent with no inhibitory effect of the amide additives because amide functionality interacts with only one carboxyl group of the polymer by the same eight-membered hydrogen bonding wherein the hydrophobic domain should not be enough to isolate the hydrophilic domain.

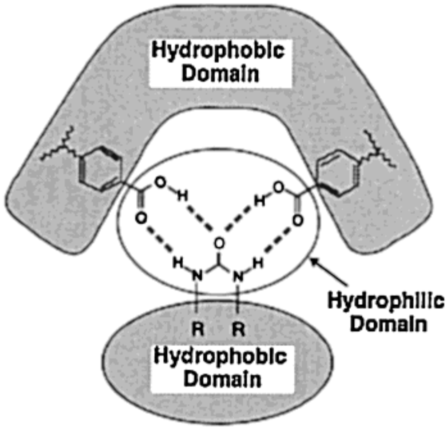


Figure 3. Supramolecular structure model for inhibitory effect of 1,3-disubstituted urea additives. A urea functionality participates in hydrogen bonding with two carboxyl groups of the polymer to form a hydrophilic domain. The hydrophobic walls consisting of the hydrophobic substituents of urea derivatives and polymer backbones surround the hydrophilic domain.

This supramolecular model is further supported by the dissolution behavior of the polymer film containing **Ur9**; the film gave a dissolution rate of 0.41 μm/min, which was similar to rates of **Ur6** and **Ur7** (Figure 2). The dissolution rate of the film containing **Ur9** was 5 times faster than **Ur1** even though **Ur9** has two additional methyl groups on one phenyl group in **Ur1**. We interpret the dissolution results by taking into account three different rotational isomers of 1,3-disubstituted ureas: syn−syn, syn−anti, and anti−anti, differentiated by the relative orientation of the NH bonds and the central carbonyl group (Scheme 3). Urea additives must take a syn−syn conformation in the supramolecular model. However, substituents of **Ur9** are too bulky to take the syn−syn conformation due to the steric repulsion of the two substituents; thus, **Ur9** should exist in the syn−anti or anti−anti conformer, which results in less dissolution inhibition of the polymer.[13,14]

Infrared Spectra of PAE Films Containing Ureas. If the supramolecular structure, in which urea compounds exist as a syn−syn conformer, is required for the dissolution inhibition of the PAE films, the syn−syn conformation must be observed in **Ur1** films but not in **Ur9** films. There have been several reports that the syn form of urea compounds was differentiated from the anti form observed in the spectral region (1600−1700 cm^{-1}) attributed to carbonyl stretching, as seen in amide compounds.[15] Therefore, we compared the infrared spectra of **Ur1** and **Ur9** in a polyamic acid film (the polymer spectrum was subtracted from each film).[16]

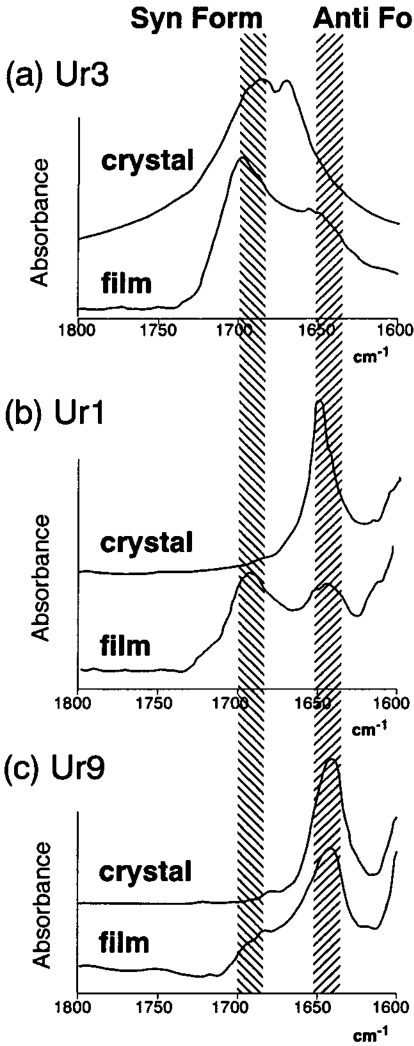
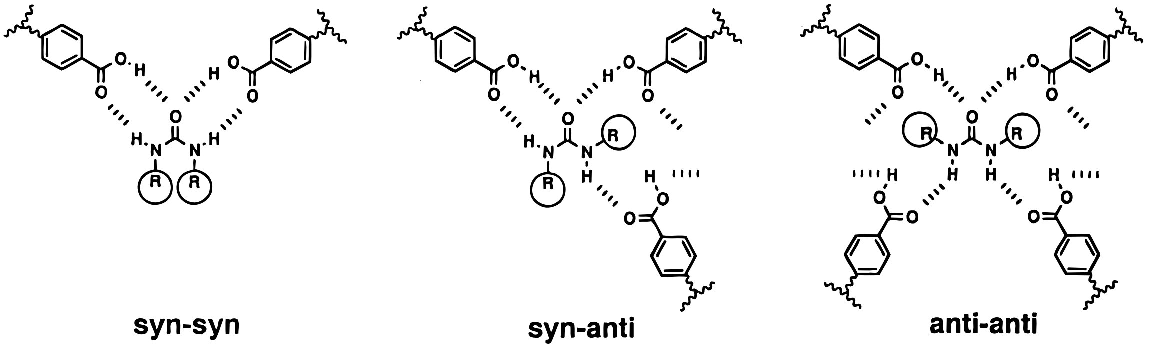


Figure 4. Infrared spectra of **Ur3** (a), **Ur1** (b), and **Ur9** (c) in the crystalline state and in the polymer film (the polymer spectrum was subtracted from each film). The bands in the regions at 1640−1650 and 1690−1700 cm^{-1} were assigned to syn−syn and anti−anti forms, respectively.

The infrared bands in the region 1600−1800 cm^{-1} of **Ur1** and **Ur3**, whose conformations in the crystalline state are known, are depicted in Figure 4a,b. **Ur3**, which exists only in the syn−syn conformer due to its cyclic structure, showed carbonyl bands at 1670 and 1685 cm^{-1} in the crystalline state and at 1695 cm^{-1} in the polymer film. The slight difference between the carbonyl bands (10 cm^{-1}) could be caused by different hydrogen-bonding interactions; namely, hydrogen bonding with the neighboring molecules of **Ur3** in the crystalline state

Scheme 3



and with the carboxyl groups of the polymer in the film. Since a crystal structure of **Ur1** has been reported wherein **Ur1** exists as the anti−anti conformer,[17] the carbonyl band, appearing at 1650 cm^{-1}, was assigned to an anti form (Figure 4b). These results indicated that the syn form and the anti form appeared in regions of 1640−1650 and 1690−1700 cm^{-1}, respectively.

In contrast to the crystalline state, **Ur1** had two carbonyl bands at 1650 and 1695 cm^{-1} in the polymer film (Figure 4b). Since the band with larger intensity at 1695 cm^{-1} can be attributed to the syn form, **Ur1** has the syn−syn conformer as the main conformer in the polymer film. This infrared spectrum suggests that **Ur1** takes part in a supramolecular structure with the carboxyl group of the polymer. While we have not carried out a crystal structure analysis of **Ur9**, we could assume that **Ur9** should take the anti−anti conformation in the crystalline state in accordance with the detailed study of 1,3-diarylureas by Etter's group.[18] In contrast to **Ur1**, the carbonyl bands of **Ur9** appear at similar wavenumbers in the crystalline state (1648 cm^{-1}) and in the film (1645 cm^{-1}) as shown in Figure 4c. Since the syn form of **Ur9** appears as a small shoulder at 1680 cm^{-1}, very few **Ur9** molecules exist in the syn−syn conformation, which was necessary for the dissolution inhibition of the polymer. The infrared spectroscopic result was in good agreement with the fact that only **Ur1** exhibited a strong inhibition of the film dissolution; namely the strong inhibitory effect should result from the syn−syn conformer of the 1,3-disubstituted urea compounds as depicted in the supramolecular structure model (Figure 3).

Conclusions

Urea derivatives lowered the dissolution rate of the polymer film more than the other carbonyl compounds such as amide, imide, and ester derivatives did. 1,3-Diphenylurea inhibited the dissolution of the polymer film more efficiently than other urea derivatives. From structural studies, a supramolecular structure model was proposed to explain this observation. The existence of such a supramolecular structure is supported by the infrared spectra of the urea additives. Designing a supramolecular structure by selecting appropriate hydrophilic groups for the polymers and the additives is a promising approach for changing dissolution behavior of polymer films. This approach should be applicable to designing tailor-made photoactive compounds for the base polymers of new photosensitive resin systems.

Experimental Section

Infrared spectra were measured on Nicolet I-5040 spectrometer. Gel permeation chromatography was performed at 30 °C with two Hitachi Chemical GL-S340 columns with an elution of tetrahydrofuran/dimethylformamide (50/50 v/v) and phosphoric acid/lithium bromide (0.6 mmol/L) at a flow rate of 1.0 mL/min. The number- and weight-average molecular weights of the polymers (M_n, M_w) were calculated on the basis of a standard polystyrene calibration.

Additives and monomers were obtained from Aldrich, Wako Pure Chemical Industries, Ltd., and Tokyo Chemical Industry Co., Ltd. Polyamic acid butyl ester with a pendant carboxyl group (PAE) was prepared from a condensation reaction between benzophenone−tetracarboxylic acid dibutylester dichloride and diamines in NMP by a conventional synthetic method for polyamic acid esters (M_n, M_w: 12 000, 20 000).[19] Polyamic acid consisting of bis(3,3′,4,4′-tetracarboxyphenyl)ether tetracarboxylic dianhydride (ODPA) and bis(4-diaminodiphenyl)ether (DDE) as monomer units was prepared by a condensation reaction between ODPA and DDE according to the conventional synthetic method (M_n, M_w: 13 000, 26 000).[20]

Each carbonyl additive was added as 0.5 equimolar to the carboxyl group of the polymer in γ-butyrolactone or NMP. PAE films were coated on silicon wafer with 1−2 μm thickness. The polymer films were immersed into 0.262 N aqueous tetramethylammonium hydroxide, which is a commercially available developer. Dissolution rates of the polymer films were determined by measuring the time for complete dissolution of the immersed films.

The calculations of a logarithmic partition coefficient of 1-octanol−water (log *P*) and molecular volumes were performed using atomic parameters derived by Ghose et al.[7] and by Bodor,[21] as implemented in the program HyperChem Pro 5.1 installed on a SGI 320 workstation.[22]

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(13) The syn−syn conformer of urea additives in our model is not in agreement with the conformational studies of ureas in solution reported by Thummel et al.[14] wherein 1,3-disubstituted ureas exist in the syn−anti form as a stable conformer in the complex with pyridyl−indole host molecules. The opposite conformer of urea compounds as the stable state should be explained by two differences between our study and Thummel's: (i) different states (film and solution); (ii) different hydrogen-bonding counterparts of the urea functionality (two carboxyl groups and two pyridyl−indole functionalities).

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