One-pot exchange reaction of acyl hydrazone combined with radical polymerization of styrene derivatives bearing acyl hydrazone moieties

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ABSTRACT: We developed a one-pot reaction combining an exchange reaction of the benzylidene moiety in an acyl hydrazone with styrene radical polymerization. The one-pot reaction of a styrene derivative bearing a 4-(dimethylamino) benzylidene acyl hydrazone moiety was conducted in the presence of 4-cyanobenzaldehyde and pyridinium *p*-toluene sulfonate/H₂O for the exchange reaction and AIBN as the radical polymerization initiator in *N*,*N*-dimethylformamide at 70 °C for 20 h. The exchange reaction proceeded quantitatively, with the 4-(dimethylamino)benzylidene acyl hydrazone moiety being

exchanged with 4-(methoxy)benzylidene acyl hydrazone, and polymerization proceeded smoothly to provide the corresponding polymer in 70% yield. Compared to traditional stepwise methods and polymer post-polymerization modifications, this one-pot system exhibits distinct advantages for the facile and efficient preparation of various functional polymers. © 2019 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**

KEYWORDS: Aldehydes; Polymers; Polymerization; Synthetic methods

INTRODUCTION Performing multiple reactions simultaneously or in tandem with polymerization is a new integrated synthetic strategy to achieve polymers with unique functionalities.^{1–3} The combination of different reactions in a one-pot system not only avoids tedious intermediate purification steps but also provides a powerful and exquisite strategy for sophisticated polymer synthesis and modification.^{4–8} One-pot processes have been achieved by the combination of selected compatible reactions with polymerizations running in parallel, leading to polymers with predesigned functionalities and structures.

For example, Sawamoto et al. combined metal-alkoxide-catalyzed transesterification with ruthenium-catalyzed living radical polymerization to efficiently produce sequence-regulated polymers in a one-pot fashion.^{9,10} Haddleton et al. developed a novel one-pot methodology through the combination of copper-catalyzed azidealkyne cycloaddition and atom transfer radical polymerization to prepare polymers bearing various functional groups.⁶ Endo et al. reported a one-pot reaction combining carbon dioxide fixation of oxirane side-chain groups with radical polymerization.¹¹ One-pot strategies consisting of three-component reactions (Bignelli reaction, Kabachnik–Fields reaction) and reversible addition–fragmentation chain transfer (RAFT) processes have also been reported to afford polymers with various functional groups.^{12–14} These successful efforts enrich and extend the content of polymer chemistry. Due to these facile, versatile, and powerful features,

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the one-pot combination of polymerization and various compatible organic reactions to achieve polymers with the desired functions is attracting more and more attention and is becoming an important research topic for the development of polymerization methodologies.

Acyl hydrazones are stable under a wide range of conditions, yet undergo covalent exchange reactions in the presence of acid/water and aldehydes.¹⁵ Acyl hydrazones are hydrolyzed by acid/water catalysts to yield hydrazide and aldehydes, and the formed hydrazide can then react with another aldehyde to afford a new acyl hydrazone exchanged at the benzylidene moiety. This reaction can tolerate radical polymerization conditions. Thus, we were encouraged to combine the exchange reaction of acyl hydrazone with radical polymerization to develop new one-pot methodologies for functional polymer syntheses.

Our one-pot synthetic strategy involves an *in situ* acyl hydrazone exchange reaction accompanied by radical polymerization as shown in Scheme 1.

EXPERIMENTAL

Materials and Instruments

4-Vinylbenzoic acid (Tokyo Kasei Kogyo, >97.0%), anhydrous hydrazine (Tokyo Kasei Kogyo, >98.0%), and 4-dimethylbenzaldehyde (Tokyo Kasei Kogyo, >99.0%) were used as received.





exchangeable group

SCHEME 1 One-pot reaction combining exchange reaction of acyl hydrazone with radical polymerization. [Color figure can be viewed at wileyonlinelibrary.com]

4-Methoxybenzaldehyde (Tokyo Kasei Kogyo, >99.0%) was distilled prior to use. 4-Cyanobenzaldehyde (Tokyo Kasei Kogyo, >98.0%) and 4-nitrobenzaldehyde (Tokyo Kasei Kogyo, >95.0%) were recrystallized from methanol. 2,2'-Azobis(isobutyronitrile) (Tokyo Kasei Kogyo, >98.0%) was used as received. Sulfuric acid (Wako Pure Chemical, >95.0%), hydrochloric acid (Wako Pure Chemical, >37.0%), and acetic acid (Kanto Chemical, >99.7%) were used as received. Dichloromethane (Wako Pure Chemical, >99.5%), methanol (Wako Pure Chemical, >99.8%), and sodium sulfate (Kanto Chemical, >99.0%) were used as received. Trifluoroacetic acid (Wako Pure Chemical, >99.5%) was distilled prior to use. Pyridinium p-toluenesulfonate (PPTS, Tokyo Kasei Kogyo, >98.0%) was recrystallized from methanol. N,N-Dimethylformamide (DMF, Tokyo Kasei Kogyo, >99.5%) was dried over calcium hydride (Aldrich, >95%) and distilled prior to use.

IR spectrum was recorded using a TheremoFisher Scientific Nicolet iS50 spectrometer and the values were given in cm^{-1} . ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III HD500 spectrometer using tetramethylsilane (TMS) as an internal standard; the δ values are reported in parts per million (ppm). Number-average (M_n) and weight-average (M_w) molecular weights were estimated by size-exclusion chromatography (SEC) using a system consisting of a Hitachi L-7100 pump, a Hitachi L-7400 refractive index (RI) detector, and polystyrene gel columns (Tosoh TSK gels α-2500, α-3000, and α -6000, with size exclusion limitations of 1×10^4 , 1×10^5 , and 1×10^7 , respectively). MALDI TOF mass spectrometric measurements were performed using an AXIMA Performance instrument (Shimadzu Co.) equipped with a nitrogen laser (λ = 337 nm). The spectrometer was operated in linear and reflection-positive ion modes with pulsed ion extraction. Samples were in tetrahydrofuran (100 mg mL⁻¹) and 2 μ L of aliquot of the mixture was deposited onto the sample target plate.

Synthesis of Methyl 4-Vinylbenzoate

Sulfuric acid (4 mL) was added dropwise to a methanol solution (160 mL) containing 4-vinylbenzoic acid (4.0 g, 27 mmol) at 0 °C. After addition, the mixture was stirred with refluxing for 17 h and a 10% aqueous solution of sodium hydrogen carbonate (240 mL) was added for neutralization. The products were extracted using dichloromethane (160 mL \times 3). The

organic laver was dried over sodium sulfate for 4 h and then filtered. The filtrate was concentrated under reduced pressure, and the residue was dried under vacuum to obtain methyl 4-vinyl benzoate as a white powder in 89% yield.

¹H NMR (500 MHz, DMSO- d_6) δ 3.84 (s, 3H), 5.43 (dd, 1H), 6.00 (dd, 1H), 6.82 (dd, 1H), 7.62 (d, 2H), 7.93 (d, 2H). ¹³C NMR (500 MHz, DMSO-d₆) δ 52.1, 117.4, 126.4, 128.8, 129.5, 135.7, 141.7, 166.0.

Synthesis of 4-Vinylbenzhydrazide

Anhydrous hydrazine (0.762 mL, 28 mmol) was added dropwise to a methanol (10 mL) solution containing methyl 4-vinylbenzoate (3.24 g, 20.0 mmol). The mixture was stirred with refluxing for 17 h and concentrated under reduced pressure. The residue was dissolved in dichloromethane (40.0 mL), dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure, and the residue was dried under vacuum to obtain the mixture containing 4-vinylbenzhydrazide and methyl 4-vinylbenzoate (99:1), which was used in the subsequent reaction.

¹H NMR (500 MHz, DMSO- d_6) δ 4.49 (s, 2H), 5.34 (dd, 1H), 5.94 (dd, 1H), 6.77 (dd, 1H), 7.54 (d, 2H), 7.80 (d, 2H), 9.77 (s, 1H). ¹³C NMR (500 MHz, DMSO-d₆) δ 117.4, 126.4, 128.8, 129.5, 135.7, 141.7, 162.2.

Synthesis of Styrene Derivative Bearing 4-(Dimethylamino)Benzilidene Acyl Hydrazone

4-Dimethylbenzaldehyde (0.46 g, 3.08 mmol) was added to a solution of methanol (56 mL) and acetic acid (3.7 mL). After stirring for 19 h at room temperature, the resulting mixture was concentrated under reduced pressure and the residue was dissolved in N,N-dimethylformamide (25.0 mL). The solution was added to distilled water (500 mL) and stirred for 3 h, and the precipitates were filtered. The precipitates were recrystallized from tetrahydrofuran/hexane (v/v = 1/2) to give the styrene derivative bearing a 4-(dimethylamino) benzylidene acyl hydrazone moiety (SDA) as white crystals in 55% yield.

¹H NMR (500 MHz, DMSO-d₆) δ 2.98 (s, 6H), 5.39 (dd, 1H), 5.96 (dd, 1H), 6.62-6.87 (m, 3H), 7.42-7.98 (m, 6H), 8.26 (s, 1H), 11.50 (s, 1H). ¹³C NMR (500 MHz, DMSO-d₆) δ 40.0, 111.5, 116.0, 120.9, 126.3, 127.4, 129.3, 132.6, 135.8, 140.8, 149.2, 151.8, 163.3. MS (MALDI-TOF MS) m/z 293.47 (calcd for M: 293.36).

One-Pot Reaction Combining Exchange Reaction of Acyl Hydrazone with Radical Polymerization of a Styrene **Derivative Bearing an Acyl Hydrazone Moiety**

SDA (200 mg, 0.680 mmol), 2,2'-azobis(isobutyronitrile) 0.0207 mmol), 4-cyanobenzaldehyde (178 mg, (3.40 mg, 1.36 mmol), DMF (0.650 mL), distilled water (6.00 µL, 0.333 mmol), and PPTS (6.00 mg, 0.04 mmol) were fed into a glass ampule. The ampule was cooled, degassed, sealed, and heated at 70 °C for 20 h. The mixture was poured into ethanol (60 mL), and the resulting precipitate was collected by suction

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filtration and dried under vacuum to obtain the corresponding polymer in 70% yield as a white powder. SEC analysis (eluent: DMF containing 0.01 M LiBr, polystyrene standards) of the formed polymer was carried out to estimate the number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) ($M_n = 6900$, $M_w/M_n = 2.09$).

¹H NMR (500 MHz, DMSO- d_6) δ 0.78–2.12 (br, 3H), 2.90 (s, 0.01 × 6H), 6.25–8.21 (br, 8H), 8.42 (br, s, 1H), 11.58 (br, s, 1H).

RESULTS AND DISCUSSION

A styrene derivative bearing 4-(dimethylamino)benzylidene acyl hydrazone (SDA) was synthesized in three steps (Scheme 2). 4-Vinylbenzoic acid was reacted with methanol in the presence of sulfuric acid to afford methyl 4-vinylbenzoate in 74% yield. The reaction of methyl 4-vinylbenzoate with anhydrous hydrazine in methanol under reflux for 18 h afforded a 99:1 mixture of 4-vinylbenzhydrazide and methyl 4-vinylbenzoate. The mixture was then reacted with 4-dimethylaminobenzaldehyde in the presence of acetic acid. Recrystallization of the resulting mixture from tetrahydrofuran and hexane removed methyl 4-vinylbenzoate to provide the styrene derivative bearing 4-(dimethylamino)benzylidene acyl hydrazone (SDA). The ¹H NMR spectra of SDA and the starting materials are shown in Figure 1. In the ¹H NMR spectrum of SDA, no signals corresponding to the two amino groups of 4-vinylbenzhydrazide (E and F) and the aldehyde group of 4-dimethylaminobenzaldehyde (P) were observed.

In order to carry out the one-pot exchange reaction of acyl hydrazone/radical polymerization successfully, the exchange reaction must not affect the progress of the radical polymerization. Radical polymerization of 4-vinylbenzaldehyde has been reported to proceed in a controlled manner, showing that aldehydes formed by hydrolysis are tolerant to the



SCHEME 2 Synthesis of styrene derivative bearing 4- (dimethylamino)benzylidene acyl hydrazone.



FIGURE 1 ¹H NMR spectra (CDCl₃, rt) of 4-vinylbenzhydrazide, SDA, and 4-(dimethylamino)benzaldehyde. [Color figure can be viewed at wileyonlinelibrary.com]

radical polymerization conditions. Primary amine groups of hydrazides are prone to nucleophilically attack toward vinyl groups of styrene derivatives. Our strategy to overcome this problem was to transfer the equilibrium to the formation of the new acyl hydrazone moiety by tuning the electronic properties of the aldehyde exchanged in the system. Thus, the excellent tolerance of many functional groups during radical polymerization allows for its combination with the exchange reaction of acyl hydrazone.

The one-pot reaction of SDA was carried out in the presence of 4-methoxybenzaldehyde and trifluoroacetic acid/H₂O for the exchange reaction and AIBN as the radical polymerization initiator in DMF at 60 C for 20 h (Scheme 3). 4-Methoxybenzaldehyde was selected as the aromatic aldehyde to be exchanged, because the methoxy group is less electron donating than the dimethylamino group, thus leading to higher electrophilicity of the carbonyl group. The nucleophilic attack of hydrazide on 4-methoxybenzaldehyde predominates that on 4-dimethylaminobenzaldehyde formed *in situ*. The



SCHEME 3 One-pot reaction combining exchange reaction of acyl hydrazone with radical polymerization of SDA. [Color figure can be viewed at wileyonlinelibrary.com]





FIGURE 2 ¹H NMR spectrum of the obtained polymer (DMSO- d_6 , rt).

polymerization proceeded smoothly to afford the corresponding polymer in 84% yield, whose M_n and M_w/M_n values were estimated to be 12,300 and 1.90, respectively. The ¹H NMR spectrum of the obtained polymer contained peaks assignable to the methoxy protons, and the integrated intensity ratio of the methoxy group to the dimethyl amino group was 84:16 (Fig. 2), indicating that the 4-(dimethylamino)benzylidene acyl hydrazone moiety was exchanged with 4-(methoxy)benzylidene acyl hydrazone with 84% efficiency (Table 1, entry 1).

To enhance the exchange efficiency of the side-chain reaction, the effect of substituents on the aromatic aldehyde was examined. Instead of 4-methoxybenzaldehyde, the utilization of aromatic aldehydes bearing electron-withdrawing groups such as cyano and nitro groups at the *para* position increased the exchange efficiency (entries 2 and 3 in Table 1). This indicates that electron-withdrawing groups increase the electrophilicity of the carbonyl group on the aromatic aldehyde. This accelerates the electrophilic attack on the carbonyl groups by the hydrazides formed *in situ*, providing a higher exchange efficiency.

Because the acidity of trifluoroacetic acid is very high ($pK_a = 0.23$), a diversity of reaction conditions cannot be tolerated. Acidic hydrolysis restricts the application of the one-pot reaction to the synthesis of various functional polymers. Therefore, utilization of the less acidic acetic acid ($pK_a = 4.76$) and pyridinium *p*-toluene sulfonate (PPTS, $pK_a = 5.21$) for the one-pot reaction was examined. The one-pot reaction in the presence of acetic acid/H₂O decreased the exchange efficiency (entry 4), suggesting that the lower hydrophobicity reduced the affinity for the organic reaction (i.e., the catalytic activity in DMF). On the other hand, although the exchange reaction proceeded quantitatively in the presence of PPTS/H₂O, polymerization did not occur (entry 5). This is because the added amount of powdery PPTS was very large (342 mg) relative to that of SDA (200 mg), which created a heterogeneous system in DMF (0.65 mL) that inhibited polymerization. In order to promote both polymerization and the exchange reaction, the effect of the concentration of PPTS was examined (Fig. 3). When the concentration of PPTS was reduced from 0.24 M to 0.12 M, polymerization did not occur due to heterogeneity, while the exchange reaction proceeded quantitatively. On the other hand, when the PPTS concentration was reduced to 0.06 M, both polymerization and the exchange reaction proceeded (42% yield of polymer and 99% exchange efficiency). Further reductions in PPTS concentration to 0.03 and 0.015 M decreased the exchange efficiency to 98%, while the polymerization yields were nearly constant. The lower concentrations of PPTS suppress the hydrolysis of the imine groups of SDA and the formation of the new acyl hydrazone moiety. These results indicate that the optimal concentration of PPTS is 0.06 M.

In order to further enhance polymerization, the effects of water and reaction temperature were examined (Table 2). Because water is a poor solvent for polymerization, its concentration was reduced. Decreasing the water concentration from 3.24 M to 1.63 and 0.81 M allowed polymerization to occur with similar yields (38–42%, entries 1–3). However, the exchange efficiency decreased, indicating that the reduction in the water concentration suppressed the hydrolysis of the imine groups of SDA and the formation of the new acyl hydrazone moiety. Finally, the effect of temperature was examined. Increasing the reaction temperature from 60 to 70 °C increased the yield of the polymer (70%) while maintaining the high exchange efficiency (99%, entry 4). However, further increasing the reaction temperature decreased

TABLE 1 One-Pot Reaction Combining Exchange Reaction	n of Acyl Hydrazone with Radical Polymerization of SDA ^a
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Entry	х	Acid	$M_{\rm n} (M_{\rm w}/M_{\rm n})^{\rm b}$	Yield/% ^c	X/SDA ^d
1	OMe	TFA	12,300 (1.90)	84	84/16
2	CN	TFA	9100 (1.18)	43	97/3
3	NO ₂	TFA	4900 (1.29)	27	99/1
4	CN	Acetic acid	13,800 (2.93)	85	41/59
5	CN	PPTS	-	-	_e

^a Conditions: $[SDA]_0 = 1.0 \text{ M}$; $[aromatic aldehyde]_0 = 2.0 \text{ M}$; $[AIBN]_0 = 3 \text{ mol}$ % to SDA; $[acid]_0 = 1.92 \text{ M}$; $[H_2O]_0 = 0.5 \text{ M}$; reaction temperature = 60 °C; reaction time = 20 h.

^c Ethanol insoluble parts. ^d Determined ¹H NMR analysis.

^e Monomer was exchanged quantitatively.

^b Estimated by SEC analysis (eluent: *N*,*N*-dimethylformamide, polystyrene standards).

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Entry	H ₂ O (M)	Temp (°C)	$M_{\rm n} \left(M_{\rm w}/M_{\rm n} ight)^{\rm b}$	Yield (%) ^c	X/SDA ^d			
1	3.25	60	7700 (1.90)	42	>99/>1			
2	1.63	60	8800 (1.85)	40	98/2			
3	0.81	60	7300 (0.81)	36	98/2			
4	3.25	70	6900 (2.09)	70	99/1			
5	3.25	80	4500 (1.99)	33	97/3			

TABLE 2 Effects of Water Concentration and Reaction Temperature in the One-Pot Reaction Combining Exchange Reaction of Acyl Hydrazone with Radical Polymerization of SDA in the Presence of PPTS/H₂O catalyst^a

^a Conditions: [SDA]₀ = 1.0 M; [4-cyanobenzaldehyde]₀ = 2.0 M;

 $[AIBN]_0 = 3 \text{ mol}\%$ to SDA; $[PPTS]_0 = 0.06 \text{ M}$; reaction time = 20 h.

^b Estimated by SEC analysis (eluent: *N*,*N*-dimethylformamide, polystyrene standards).



FIGURE 3 Effect of concentration of PPTS in one-pot reaction combining exchange reaction of acyl hydrazone with radical polymerization of SDA. Conditions: $[SDA]_0 = 1.0 \text{ M}$; [4-cyanobenzaldehyde]_0 = 2.0 M; [AIBN]_0 = 3.0 mol % to SDA; $[H_2O]_0 = 0.5 \text{ M}$; reaction temperature = 60 °C; reaction time = 20 h.



FIGURE 4 Kinetic study of one-pot reaction combining exchange reaction of acyl hydrazone with radical polymerization of SDA. Conditions: $[SDA]_0 = 1.0 \text{ M}$; $[4\text{-cyanobenzaldehyde}]_0 = 2.0 \text{ M}$; $[AIBN]_0 = 3.0 \text{ mol} \%$ to SDA; $[H_2O]_0 = 0.5 \text{ M}$; reaction temperature = 70 °C; reaction time = 20 h.

ADVANCED SCIENCE NEWS ^c Ethanol insoluble parts.

^d Determined ¹H NMR analysis.

both the polymer yield (33%) and exchange efficiency (97%). The high temperature disturbed the equilibrium, thus affecting the formation of the new acyl hydrazone moiety. Therefore, the optimal conditions in the one-pot reaction were determined to be: $[SDA]_0 = 1.0 \text{ M}$; $[4\text{-cyanobenzaldehyde}]_0 = 2.0 \text{ M}$; $[AIBN]_0 = 3.0 \text{ mol }\%$ to SDA; $[PPTS]_0 = 0.06 \text{ M}$; $[H_2O]_0 = 0.5 \text{ M}$; reaction temperature = 70 °C; reaction time = 20 h.

Reaction monitoring under the optimal conditions revealed that the exchange reaction for the acyl hydrazone moiety was faster than polymerization (Fig. 4). The acid-catalyzed acyl hydrazone exchange reaction proceeded with an efficiency of 45% within 3 min, at which point polymerization had only achieved 34% conversion of SDA. The exchange reaction then accelerated with the efficiency reaching 100% within 10 min, while polymerization was at 36% conversion. Polymerization continued gradually under these reaction conditions and reached a plateau of 70% conversion at 10 h. These results suggest that the one-pot reaction is essentially composed of two stages. In the first stage, the exchange reaction of the benzylidene moiety in the acyl hydrazone of SDA is fast due to the lower steric hindrance, forming the new monomer, the styrene derivative bearing the 4-(cyano)benzylidene acyl hydrazone. The second stage is homopolymerization of the new monomer, which is considerably slower.

CONCLUSIONS

A new horizon with regard to acyl hydrazone exchange reactions in polymer chemistry is presented. Through a one-pot strategy, the exchange reaction of the benzylidene moiety in an acyl hydrazone was found to be compatible with radical polymerization. The one-pot reaction of a styrene derivative bearing a 4-(dimethylamino)benzylidene acyl hydrazone moiety was conducted in the presence of 4-cyanobenzaldehyde and pyridinium *p*-toluene sulfonate/H₂O for the exchange reaction and AIBN as the radical polymerization initiator in DMF at 70 °C for 20 h. Polymerization proceeded smoothly to afford the polystyrene derivative bearing 4-(cyano) benzylidene acyl hydrazone moieties in 70% yield and with 99% exchange efficiency. Compared to traditional stepwise methods and polymer post-polymerization modifications, this one-pot system exhibits distinct advantages for the facile and efficient preparation of polymers bearing various functional groups.

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