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Synthesis of polyhydrazones by diazo coupling reaction of bisacetoacetamides with diazonium salts

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Summary

Hydrazone polymers were prepared by the diazo coupling reaction of bisacetoacetamides with diazonium salts under mild basic conditions. Bisacetoacetamides **1** and **2** having two 1,3-diketo groups were prepared by the reaction of aromatic diamines with diketene. Diazonium salts **3-5** were prepared by the reaction of aromatic diamines with nitrous acid in an aqueous HCl. A diazonium salt was isolated in a stable form after exchanging chloride with fluoroborate. The resulting polymer structure was determined by spectroscopic methods to be mainly polyhydrazone. The hydrazone unit was found stabilized by the intramolecular hydrogen bonding. The polymer obtained from **2** and **5** was soluble in organic solvents and showed the UV maximum peak at 376 nm in dimethyl sulfoxide.

Introduction

A hydrazone is a tautomer of an azo compound. Since the azo and hydrazone tautomers show different optical and physical properties, their tautomerization has been extensively studied in color industries. A hydrazone tautomer is usually bathochromic compared to the azo form and often commercially preferred. And also some hydrazones are used as charge transport materials for organic photoconductors. They constitute a charge transport layer with a binder such as polycarbonate (1-3).

Hydrazone or azo compounds are generally prepared by the coupling reaction of diazonium salts with electron rich aromatic compounds. When an azo group is directly linked to an aromatic ring, a hydrazone tautomer can exist only at the cost of the resonance stabilization energy of an aromatic ring and thus tautomerization principally depends on the relative thermodynamic stabilities of the tautomers. Among aliphatic compounds, 1,3-diketo acid derivatives can undergo the diazo coupling reaction. In this case, tautomerizm between an azo and a hydrazone is greatly influenced by the intramolecular hydrogen bonding. There have been prepared azo acetoacetanilide pigments by the reaction of acetoacetanilide having a 1,3-diketo structure and various diazonium salts.

In this work, we prepared bisacetoacetamides by the reaction of aromatic diamines with diketene (4). Bisacetoacetamides have two 1,3-diketo groups. Under mild basic conditions, acidic ß-protons are easily removed to generate carbanions, which can react with bisdiazonium salts to yield azo or hydrazone polymers. Here we describe the synthesis of bisacetoacetamides and their coupling reaction with diazonium salts. The resulting polymer structure was determined by spectroscopic methods to be mainly polyhydrazone. The hydrazone unit was found stabilized by the intramolecular hydrogen bonding.

Experimental

Materials and instrumentation

All chemicals were purchased from Aldrich Chemical Co. and used without further purification. The solvents were purified by standard procedures (5). The infrared spectra were recorded by using a Midac FT-IR spectrophotometer. The UV-Vis spectra were obtained with a Hewlett-Packard HP8452A spectrometer. The ^{1}H-NMR spectra were recorded on a Jeol JNM-LA300 spectrometer. Gel permeation chromatography (GPC) was carried out with a Viscotek Model 250 equipped with a M410 refractive index detector and PL Gel Mix-B and 5μ Mix-D columns at room temperature. Tetrahydrofuran was used as an eluent. Elemental analysis was performed by a CE Instrument EA1110 analyzer.

*Synthesis of bisacetoacetamide **1***

To a solution of 4,4' -(hexafluoroisopropylidene)dianiline (1.5 g, 4.5 mmol) in DMF (3 ml) was added diketene (0.69 ml, 9.0 mmol) dissolved in DMF (3 ml). The mixture was stirred for 4 h at 80 °C. After evaporation of the solvent, the product was isolated by column chromatography on silica gel (10% of hexane in ethyl acetate) (yield: 72 %).

^{1}H-NMR(DMSO-d6): δ 10.22 (s, NH, 2H), 7.65, 7.22 (dd, phenyl proton, 8H), 3.70 (s, $COCH_2CO$, 4H), 2.21 (s, $COCH_3$, 6H). IR (KBr, cm^{-1}): 3340, 3117, 3061, 2924, 1722, 1676, 1541, 1170. Anal. Calcd for $C_{23}H_{20}F_6N_2O_4$: C, 54.98; H, 4.01; N, 5.58. Found: C, 54.94; H, 4.23; N, 5.60.

*Synthesis of bisacetoacetamide **2***

The diamine was prepared according to the literature. To a solution of 1-fluoro-4-nitrobenzene (10 ml, 54 mmol) in N,N-dimethylforamide (DMF) (10 ml) was added K_2CO_3 (11.1 g, 80 mmol) and tri(ethylene glycol) (2.67 ml, 20 mmol). The solution was stirred for 24 h at 100 °C. Dinitro, compound was obtained by precipitation of the reaction mixture into water and then recrystallization from ethanol (yield: 83%). The nitro compound (4.5 g) was hydrogenated in THF (100 ml) in the presence of Pd/C (0.15 g) under hydrogen atmosphere (5 atm) to give a diamine (yield: 100%). The reaction of the diamine with diketene proceeded by following the procedure for compound **1**. Compound **2** was isolated by column chromatography on silica gel (25% of ethyl acetate in hexane) (yield: 81 %).

^{1}H NMR (DMSO-d$_6$) δ 10.00 (s, 2H, NH), 7.55, 6.95 (dd, 8H, phenyl proton), 4.05, 3.85, 3.63 (broad, 12H, OCH_2), 3.58 (s, 4H, $COCH_2CO$), 2.24 (s, 6H, $COCH_3$). IR (KBr, cm^{-1}): 3288, 2916, 1722, 1655, 1610, 1541, 1514. Anal. Calcd for $C_{26}H_{32}N_2O_8$: C, 62.39; H, 6.44; N, 5.60. Found: C, 62.22; H, 6.59; N, 5.82.

*Synthesis of 4,4'-oxydiphenylene bisdiazonium fluoroborate (**3**)*

4,4'-Oxydianiline (1.67g, 8.34 mmol) was dissolved in 1.7 ml of 10 N hydrochloric acid and 22 ml of distilled water at 60 °C. The solution was cooled to 5 °C and then sodium nitrite (1.27g, 18.37 mmol) was added. After stirring for 1 h at 0 ~ 5 °C, sodium fluoroborate (2.02 g, 18.37 mmol) in water (5 ml) was added to the reaction mixture and the mixture was stirred for 30 min at 0 ~ 5 °C. The resulting precipitates were isolated by filtration and washed with water, methyl alcohol, diethyl ether, and dried in air (yield: 21 %).

^{1}H-NMR (DMSO-d$_6$): δ 8.80, 7.79 (dd, phenyl proton, 8H). IR (KBr, cm^{-1}): 3425, 3082, 2258, 1560, 1259, 1085.

*Synthesis of 4,4'-(butyleneglycol)diphenylene bisdiazonium fluoroborate (**4**)*

4,4'-(Buthyleneglycol)dianiline (0.35 g, 1.29 mmol) was dissolved in 0.26 ml of 10 N hydrochloric acid and 3.5 ml of distilled water at 60 °C. The solution was cooled to 5 °C and then sodium nitrite (0.20 g, 2.90 mmol) was added. After stirring for 1 h at 0

~ 5 °C, sodium fluoroborate (0.32 g, 2.90 mmol) in water (5 ml) was added to the reaction mixture and the mixture was stirred for 30 min at 0 ~ 5 °C. The resulting precipitates were isolated by filtration and washed with water, methyl alcohol, diethyl ether, and dried in air (yield: 25 %).

^{1}H-NMR (DMSO-d_6): δ 8.60, 7.47 (dd, phenyl proton, 8H), δ 4.36, 1.96 (ss, OCH_2 $CH_2CH_2CH_2O$, 8H). IR (KBr, cm^{-1}): 3379, 3081, 2253, 1579, 1278, 1084.

Synthesis of 4,4'-(hexafluoroisopropylidene)diphenylene bisdiazonium fluoroborate (5)

4,4'-(Hexafluoroisopropylidene)dianiline (1.5 g, 4.49 mmol) was dissolved in 0.9 ml of 10 N hydrochloric acid and 12 ml of distilled water at 60 °C. The solution was cooled to 5 °C and then sodium nitrite (0.68g, 9.86 mmol) was added. After stirring for 1 h at 0 ~ 5 °C, sodium fluoroborate (1.08 g, 9.86 mmol) in water (5 ml) was added to the reaction mixture and the mixture was stirred for 30 min at 0 ~ 5 °C. The resulting precipitates were isolated by filtration and washed with water, methyl alcohol, diethyl ether, and dried in air (yield: 19 %).

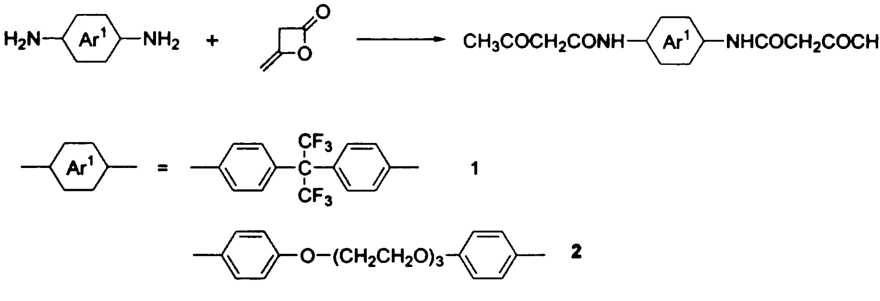
^{1}H-NMR (DMSO-d_6): δ 8.83, 8.06 (dd, phenyl proton, 8H). IR (KBr, cm^{-1}): 3437, 3088, 2287, 1583, 1257, 1084.

Synthesis of hydrazone polymers

Reaction conditions are described in Table 1. A general procedure is as follows. A two-necked flask was charged under nitrogen with equimolar of a bisacetoacetamide, bisdiazonium fluoroborate, and sodium acetate in N-methyl-2-pyrrolidinone (NMP). After stirring for 12 h at room temperature, the polymer was isolated by precipitation into distilled water. The polymer was purified by reprecipitation from the polymer solution in NMP into diethyl ether.

Results and discussion

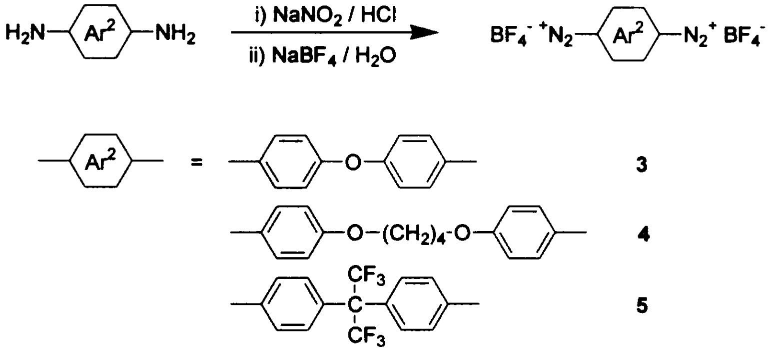
The acetoacetyl groups were introduced to diamines by the reaction with diketene (Scheme 1), resulting in bisacetoacetamides having 1,3-diketo groups at their both sides. The aromatic amines containing a bulky trifluoromethyl or flexible tri(ethylene glycol) group were used in this work to increase the solubilities. The reaction was carried out in DMF and overall yields were higher than 70%. In the ^{1}H NMR spectra, ß-proton peaks appeared at 3.70 and 3.58 ppm for compounds **1** and **2**, respectively.



Scheme 1

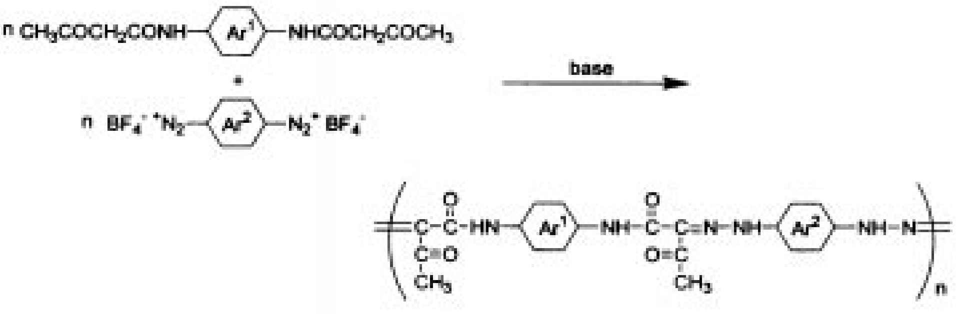
A diazonium chloride could be prepared by treatment of a diamine with nitrous acid in an aqueous HCl. Since diazonium salt is highly unstable in its dried state, we used it for the polymerization without isolation. However, the reaction gave only an oligomer. This was attributed to the stoichiometric imbalance, since diazotization was hardly accomplished in a quantitative yield.

A diazonium salt was isolated in a stable form after exchanging chloride with fluoroborate (6,7). 4.4'-Oxydiphenylene bisdiazonium fluoroborate (**3**) was prepared by the reaction 4,4'-oxydianiline with sodium nitrite in an aqueous HCl followed by treatment with sodium fluoroborate (Scheme 2). The chemical structure of **3** was confirmed by IR and ^{1}H-NMR spectroscopy. The IR spectrum exhibited characteristic absorption at 2258 cm^{-1} for N≡N stretching vibration. In the ^{1}H NMR spectrum, the peaks of benzeng ring protons appeared at 8.80 and 7.79 ppm. The NH_2 peak of 4,4'-oxydianiline at 4.80 ppm disappeared. 4,4'-(Butyleneglycol)diphenylene bisdiazonium fluoroborate (**4**) and 4,4'-(hexafluoroisopropylidene)diphenylene bisdiazonium fluoroborate (**5**) were also prepared in the same manner. All salts were only air dried before use for the polymerization.



Scheme 2

Hydrazone polymers were prepared by the diazo coupling reaction of bisacetoacetamides with bisdiazonium fluoroborate compounds according to Scheme 3. Table 1 shows polymerization conditions and results. The polymers obtained from **1** and **3**, and **1** and **4** were yellowish and insoluble in the common organic solvents such as methanol, acetone, chloroform, tetrahydrofuran, and dimethyl sulfoxide.



Scheme 3

The polymer obtained from **2** and **5** has bulky trifluoromethyl and flexible tri(ethylene glycol) groups on its backbone and was soluble in tetrahydrofuran and NMP. The polymer was isolated as a yellow powder. In the NMR spectrum, the peaks for aromatic protons at 6.9 ~ 7.9 ppm and ethoxy protons at 3.6 ~ 4.1 ppm appeared (Figure 1). There also showed up two additional peaks at 10.9 and 13.7 ppm corresponding to CONH and -C=N-NH- protons, respectively, indicating that the polymer existed almost completely in its hydrazone form in DMSO-d_6. This was also confirmed by the fact that there was not observed the peak for ß-protons which the azo tautomeric units should have (8,9). In the IR spectrum, an absorption at 1722 cm^{-1} for carbonyl stretching vibration disappeared and a new absorption at 1664 cm^{-1} appeared (Figure 2). This result strongly suggests that the hydrazone structure of the polymer was stabilized by the intramolecular hydrogen bonding (Figure 3).

Table 1. Polymerization conditions[a] and results

bisaceto-acetamide	bisdiazonium fluoroborate	Mn[b]	Mw[b]	yield (%)
1	**3**	-	-	70
1	**4**	-	-	68
2	**5**	4,570	8,580	63

[a] Polymerization was carried out in NMP (5 ml) for 12 h at room temperature by using equimolar (0.47 mmol) of a bisacetoacetamide, diazonium salt, and sodium acetate.
[b] Molecular weights were measured by gel permeation chromatography in tetrahydrofuran versus polystyrene standards.

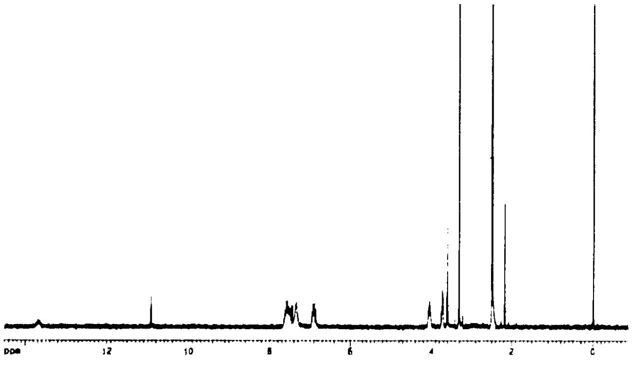


Figure 1 ^1H NMR spectrum of the polymer obtained from **2** and **5** in DMSO-d_6.

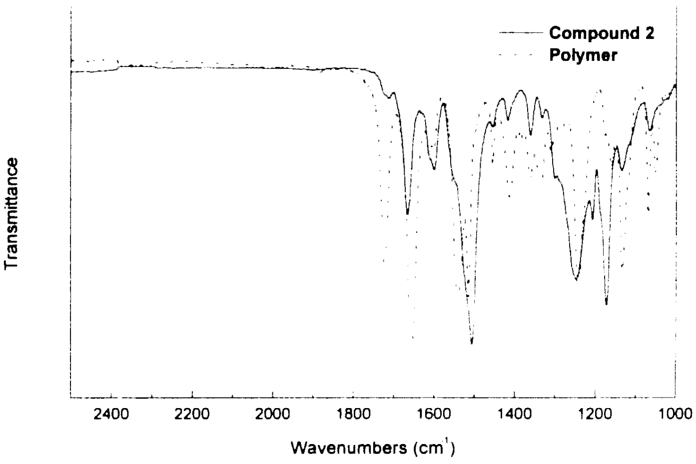


Figure 2. IR spectra of compound **2** and the polymer from **2** and **5**.

The number-average molecular weight and the weigh-average molecular weight of the polymer were determined to be 4570 and 8580 by GPC in THF. UV spectroscopy showed the maximum peak of the polymer at 376 nm in dimethyl sulfoxide.

Conclusion

We prepared hydrazone polymers by the diazo coupling reaction of bisacetoacetamides with diazonium salts under mild basic conditions. The polymer from bisacetoacetamide **2** with a flexible tri(ethylene glycol) group and diazonium **5** with bulky trifluoromethyl groups was soluble in organic solvents. Since lots of diamines are available and easily converted to the corresponding bisacetoacetamides or diazonium salts, the hydrazone polymers with various structures can be prepared and have a potential use as polymeric pigments or charge transport materials.

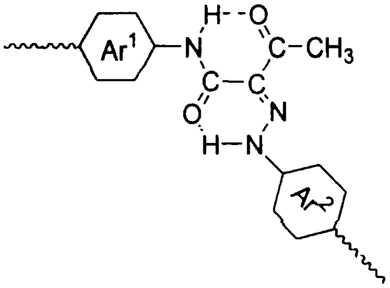


Figure 3. Hydrazone structure stabilized by the intramolecular hydrogen bonding.

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