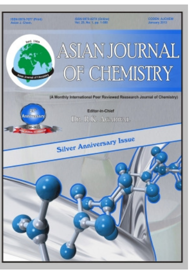
Asian Journal of Chemistry; *Vol. 25, No. 6 (2013), 3247-3251*

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13608



A Facile Synthesis of Poly(acrylanilide-*co*-acrylic Acid)

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(*Received*: 16 February 2012; *Accepted*: 14 December 2012) AJC-12558

A range of poly(acrylanilide-*co*-acrylic acid) was synthesized through a facile one-pot condensation of poly(acrylic acid) with aromatic amines. Thionyl chloride was added in a stepwise manner to N,N-dimethyl acetamide and poly(acryloyl chloride) need not be isolated during the reaction. Compared with conventional methods, the condensation of poly(acryloyl chloride) with aromatic amines could perform without the addition of other bases (such as triethylamine, pyridine, *etc*.). Regardless of electron-withdrawing or electron-donating groups the aromatic amines contain, the reaction was carried out smoothly. Different molar ratios of poly(acrylic acid) (acrylic acid units) to aromatic amines were investigated and moderate yields were obtained. The products were characterized by nuclear magnetic resonance spectroscopy and Fourier-transform infrared spectroscopy.

Key Words: One-pot synthesis, Poly(acrylanilide-*co*-acrylic acid), Thionyl chloride.

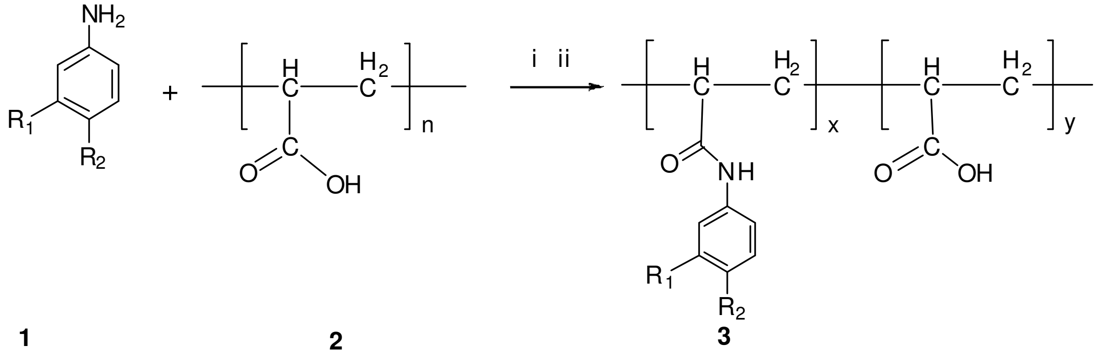
INTRODUCTION

In recent years, the aromatic amide derivatives of poly(acrylic acid) (PAAc) and poly(methacrylic acid) (PMAc) have been paid much attention because of their ease of functionalization and processing, good performance, excellent physical and chemical stability[1]. They show potential applications in biosensors and biomedical fields[2-7], drug delivery systems[8,9], detection and analytical chemistry fields[10-13] and optical materials[14-16]. These poly(methacrylamides) and poly(acrylamides) with various functional groups could be prepared by polymerization of monomers. However, it was frequently failed to attempt free radical polymerization or anionic polymerization of acrylanilides or methacrylanilides monomers, only low molecular weight oligomers were obtained and the yields were quite low, due to the influences of steric hindrance and inhibition groups (*e.g*., nitro groups)[14,15]. Therefore, there is a need to develop new strategies for synthesizing poly(acrylanilide-*co*-acrylic acid) (PAAn-*co*-AAc) polymers. Additional approaches for the synthesis of PAAn-*co*-AAc *via* the reaction of poly(methacryloyl chloride) or poly(acryloyl chloride) with aromatic amines have been applied in some reports[14,15,17]. However, due to that methacryloyl chloride, acryloyl chloride, poly(methacryloyl chloride) and poly(acryloyl chloride) are extremely moisture sensitive and readily hydrolyzed, they have to be strictly dealt with. It would be more satisfactory if PAAn-*co*-AAc could be synthesized in a one-pot condensation directly from poly(acrylic acid) without the use of reactive acryloyl chloride or poly(acryloyl chloride).

Recently, a synthesis of acrylanilides and anilides directly from acrylic acid and other organic acids using thionyl chloride which is a commonly available reagent at a relatively low cost was investigated and a high conversion was achieved[18]. To our best of knowledge, there was no report about synthesis of PAAn-*co*-AAc directly from poly(acrylic acid) using thionyl chloride. Encouraged by the formation of acryanilides using thionyl chloride in N,N-dimethyl acetamide (DMAC) at ambient temperature and also by the ability of N,N-dimethyl acetamide to dissolve both poly(acrylic acid) and aromatic amines, it is expected that the synthesis of PAAn-*co*-AAc could be achieved *via* a direct condensation of poly(acrylic acid) and aromatic amines without using reactive acryloyl chloride and poly(acryloyl chloride), so we extended this approach towards the synthesis of PAAn-*co*-AAc (**Scheme-I**).

EXPERIMENTAL

Acrylic acid, thionyl chloride, petroleum ether (boiling range 90-120 ºC) and analytical grade N,N-dimethyl acetamide were obtained from Tianjin Bodi Chemical Holding Co. Ltd. Azo-*bis*-isobutyronitrile (AIBN) was purchased from Tianjin Guangfu Fine Research Institute and was recrystallized from ethanol before use. Isopropanol was obtained from Tianjin Fuyu Fine Co., Ltd. 4-Nitroaniline was from Shanghai Kefeng Chemical Reagents Co. Ltd. and *p*-methoxyaniline was from Shanghai Auxiliaries Factory. 3-(N,N-Diethylamino)aniline was obtained from the hydrolysis of N-(3-N,N-diethylaminophenyl) acetamide according to literature[19]. Before use, N,N-dimethyl acetamide was dried using 4 Å molecular sieves.



a	**R_1=H**	**R_2=H**
b	**R_1=H**	**R_2=NO_2**
c	**R_1=H**	**R_2=OCH_3**
d	**R_1=$N(CH_2CH_3)_2$**	**R_2=H**

Scheme-I: Synthesis of P(AAn-AAc) **3a-d**. i, N,N-dimethyl acetamide, -5 ºC, $SOCl_2$; ii, aromatic amine, 20-70 ºC

4-Nitroaniline and *p*-methoxaniline were recrystallized from ethyl acetate and toluene mixture (1:2, v/v). All other reagents were used as commercially received except indicated.

Synthesis of poly(acrylic acid): Poly(acrylic acid) was prepared by precipitation polymerization in petroleum ether as already reported[20-22]. In a 250 mL three-neck flask fitted with a reflux condenser, acrylic acid (15 g, 0.208 mol) was added dropwise within 0.5 h to a stirred solution of isopropanol (15 g) and azo-*bis*-isobutyronitrile (1 g) in 100 mL petroleum ether at 80 ºC. After the addition of acrylic acid, polymerization was performed with a mechanical stirrer at 80 ºC for 3.5 h. At the completion of the reaction, the solvent was removed under reduced pressure at 90 ºC/5 mmHg and the products were withdrawn from the reactor and dried under vacuum at 50 ºC for 24 h. The average molecular weight (Mw) and the polydispersity index of poly(acrylic acid) were measured by gel permeation chromatography(GPC) at 25 ºC using deionized water as the eluent at a flow rate of 1 mL/min. Narrow disperse poly(ethylene glycol) was used as calibration standards. Molecular weight (Mw) and its distribution of the polymers were determined by gel permeation chromatography on an Agilent 1200 apparatus. And a molecular weight of 84345 g/mol and a polydispersity index of 1.93 were obtained.

General procedure for the preparation of PAAn-*co*-AAc: A solution of poly(acrylic acid) (1.8 g, 0.025 mol acrylic acid units) and dried N,N-dimethyl acetamide (25 mL) was cooled to -5 ºC in a 100 mL three-neck flask equipped with a mechanically stirrer and a scrubber containing sodium hydroxide solution. After the solution was vigorously stirred under nitrogen atmosphere for 15 min, the desired amount of thionyl chloride was added dropwise over 10 min. The solution was stirred under nitrogen at -5 ºC for another 0.5 h, then the solution was warmed up to 20 ºC and kept at this temperature for 20 min, followed by the addition of aromatic amines in 5 mL N,N-dimethyl acetamide over 15 min. Upon complete addition, the solution was stirred at 20 ºC for 20 min and then at 70 ºC for 14 h. Nitrogen was bubbled throughout the process.

A range of PAAn-*co*-AAc was synthesized and the reactions were carried out under the same procedure as described above, except that different molar ratios of poly(acrylic acid) and the aromatic amine to thionyl chloride were used. The molar ratios of aromatic amine: poly(acrylic acid) (calculated as carboxyl groups): thionyl chloride were 1.0:4.0:4.4, 2.0:4.0:4.4, 4.0:4.0:4.4, respectively. The functionalizations of all samples were defined as the molar ratio of the aromatic amine to the carboxyl group of the polymer.

The reaction solutions of **3a** were poured into 200 mL ice water. After filtration, the filter cake was washed with water until the filtrate was neutral, then vacuum dried at 30 ºC to obtain the crude products. The crudes of **3a** were washed with dichloromethane for several times until no aniline (R_f = 0.53) were detected by thin-layer chromatography (TLC *n*-petroleum ether:ethyl acetate = 1/9, v/v) then dried under vacuum at 30 ºC. Final cakes of **3c** were also obtained in the same way.

The crude products of **3b** were similarly obtained with the procedure above-mentioned for **3a**. The crude products of **3b** were dissolved in 20 mL acetone and the solutions were precipitated using 100 mL ethyl ether. The procedure was repeated 5 times to remove the residual 4-nitroaniline. Then the final cakes were dried under vacuum at 30 ºC.

The reaction solutions of **3d** were precipitated into 200 mL acetone and washed extensively with acetone to get the crude products and then vacuum dried at 30 ºC to obtain the crude products. The solution pH was adjusted to 4.5 with sodium carbonate after the crudes of **3d** were dissolved in 30 mL ice water. After filtration, the final cakes were washed with ice water until no 3-(N,N-diethylamino)aniline was detected by TLC (R_f = 0.87, *n*-petroleum ether:ethyl acetate = 1/9, v/v) and then dried under vacuum at 30 ºC.

Analytical techniques: The ^{1}H NMR spectra were recorded on a VARIAN INOVA (400 MHz) spectrometer using TMS as an internal standard. FT-IR spectra were determined on a Perkin-Elmer 983 infrared spectrometer using KBr pellets. Elemental analysis of N, O and H for the polymer samples was performed with a Vario-EL analyzer. The measurement of average molecular weight was carried on Agilent Technologies 1200 series GPC.

3a (The products of aniline to carboxyl groups 1:4, 1:2 and 1:1 (**3a-1**, **3a-2**, **3a-3**)were obtained in 91.0, 77.9 and 73.8 yield, respectively) FT-IR (KBr, ν_{max}, cm^{-1}): 3424 (NH), 1711 (C=O), 1665 (C=O amide), 1600-1400 (C=C aromatic), 1384 (CH_3), 1311 (C-N), 1250 (C-O), 755 (CH aromatic), 692 (CH aromatic). ^{1}H NMR (DMSO-d_6, δ, ppm): δ = 1.0-1.9 (m, CH_2), 2.0-2.5 (m, CH), 6.9-7.7 (m, 5H, aromatic protons), 9.5-10.1 (s, 1H, NH-CO), 12.0-12.4 (s, COOH).

3b (The **3b-1**, **3b-2** and **3b-3** were obtained in 74.4, 49.1 and 67.0 yield, respectively) FT-IR (KBr, ν_{max}, cm^{-1}): 3441 (NH), 1655 (C=O amide), 1597 (C=C aromatic), 1554 (NO_2), 1508-1449 (C=C aromatic), 1343 (C-NO_2), 1254 (C-N amide), 852 (CH aromatic). ^{1}H NMR (DMSO-d_6, δ, ppm): δ = 0.8-2.0 (m, CH_2), 2.0-2.6 (m, CH), 7.5-8.4 (m, 4H, aromatic protons), 10.3-10.8 (s, 1H, NH-CO), 11.9-12.8 (s, COOH).

3c (The **3c-1**, **3c-2** and **3c-3** were obtained in 77.5, 96.4 and 76.2 % yields, respectively) FT-IR (KBr, ν_{max}, cm^{-1}): 3445 (NH), 1721 (C=O), 1655 (C=O amide), 1511-1433 (C=C aromatic), 1384 (CH_3), 1300 (C-N), 1243-1168 (C-O-C), 826 (CH aromatic). ^{1}H NMR (DMSO-d_6, δ, ppm): δ = 1-2.0 (m, CH_2), δ = 2.0-2.6 (m, CH), δ = 3.6-3.8 (s, 3H, OCH_3), δ = 6.5-7.6 (m, 4H, aromatic protons), δ = 9.2-10.0 (s, 1H, NH-CO), δ = 11.7-12.5 (s, COOH).

3d (The **3d-1**, **3d-2** and **3d-3** were obtained in 78.9, 53.4 and 46.6 % yield, respectively) FT-IR (KBr, ν_{max}, cm^{-1}): 3428 (NH), 2972-2934 (CH), 1670-1650 (C=O amide), 1608-1600 (C=O COO- and C=C aromatic), 1578-1400 (C=C aromatic), 1176 (C-N), 860-678 (CH aromatic). ^{1}H NMR (D_2O, δ, ppm): δ = 0.7-2.4 (m, CH_2, CH_3, CHC=O and CHCO-N), δ = 2.75-3.30 (m, 4 H, CH_2-N), δ = 6.4-7.4 (m, 4H, aromatic protons).

RESULTS AND DISCUSSION

The preparation process of PAAn-*co*-AAc is shown in **Scheme-I**. FTIR spectra (Fig. 1) confirm the formation of PAAn-*co*-AAc and show significant differences between poly(acrylic acid) and PAAn-*co*-AAc. Compared the IR spectrum of poly(acrylic acid) with that of **3a**, a strong adsorption band appeared at 1714 cm^{-1}, corresponding to the stretching vibration of C=O of -COOH group, and it shows an obvious shift to lower wavenumber (1665 cm^{-1}) after the reaction of -NH_2 of aniline with -COOH of poly(acrylic acid). In addition, the new peaks at 1599, 1544 and 1498 cm^{-1} are related to the bands of the benzene ring. The polymers of **3a-d** were also characterized with ^{1}H NMR (Fig. 2). Exampled for **3a**, the signal at 1.0-2.6 ppm stands for the proton on the polymer backbone. The peaks at 6.5-7.6 ppm are ascribed to aromatic protons H-1, H-2 and H-3. The signal at 9.7 ppm stands for the amide proton H-4 and the signal at 12.2 ppm stands for the carboxylic acid proton. These results indicated that poly(acrylic acid) was successfully transformed to the polyamide during reaction. In addition, for **3d** it was worthy to note that the signal of its amide and carboxylic acid proton didn't show in D_2O.

The functionalization (F %) of PAAn-*co*-AAc was calculated on the basis of nitrogen content (N %) determined with the elemental analyses (eqn. 2):

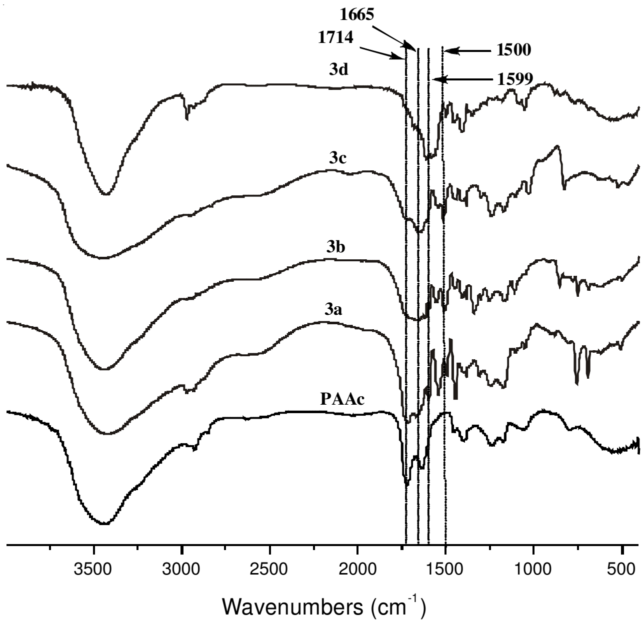


Fig. 1. FTIR spectra of poly(acrylic acid), **3a**, **3b**, **3c** and **3d**

$$N\ (\%) = \frac{14n \times F\ \%}{72 + F\ \%(M - 18)} \quad (1)$$

$$F\ (\%) = \frac{72 \times N\ \%}{14n - N\ \%(M - 18)} \quad (2)$$

where M is the mass of aromatic amine and n represents the number of nitrogen of the corresponding aromatic amine bearing. 14 and 72 are the mass of nitrogen atom and repeated chain unit of poly(acrylic acid) polymer, respectively. 18 is the molecular weight of water generated during condensation.

The reaction was optimized by varying the molar ratio of aromatic amine to poly(acrylic acid) (acrylic acid units) and the reaction temperature. Although 1 mol of thionyl chloride should give rise to 1 mol of acryloyl chloride, it proved best to use an excessive quantity of thionyl chloride. Condensation of aromatic amine with poly(acrylic acid) required higher temperature (70 ºC) than that with acrylic acid (25-50 ºC)[18], this may be due to the higher viscosity and steric hindrance of the polymer.

The functionalization (F %) results of the synthesized PAAn-*co*-AAc samples were summarized in Table-1. It showed that the molar ratio of the aromatic amine to carboxyl group of poly(acrylic acid) played an important role in the functionalization of PAAn-*co*-AAc. As the molar ratio of aniline to carboxyl group increased from 1:4 to 1:2, the F % of PAAn-*co*-AAc increased from 24.1 to 39.1 %. When the molar ratio further increased to 1:1, the F % of PAAn-*co*-AAc increased to 52.7 %. It can be seen from the results that with the increase of dosage of aniline, the conversion of aniline decreased, which is probably due to steric hindrance from the benzene ring introduced. A comparison of F % of the other samples with different aromatic amines was also made to show the same result. It indicated that once its neighbored unit of poly(acrylic acid) was already functionalized, acrylic acid unit was more difficult to be functionalized by aromatic amine molecules. Except aniline, *p*-nitro (**1b**), *p*-methoxy (**1c**) and

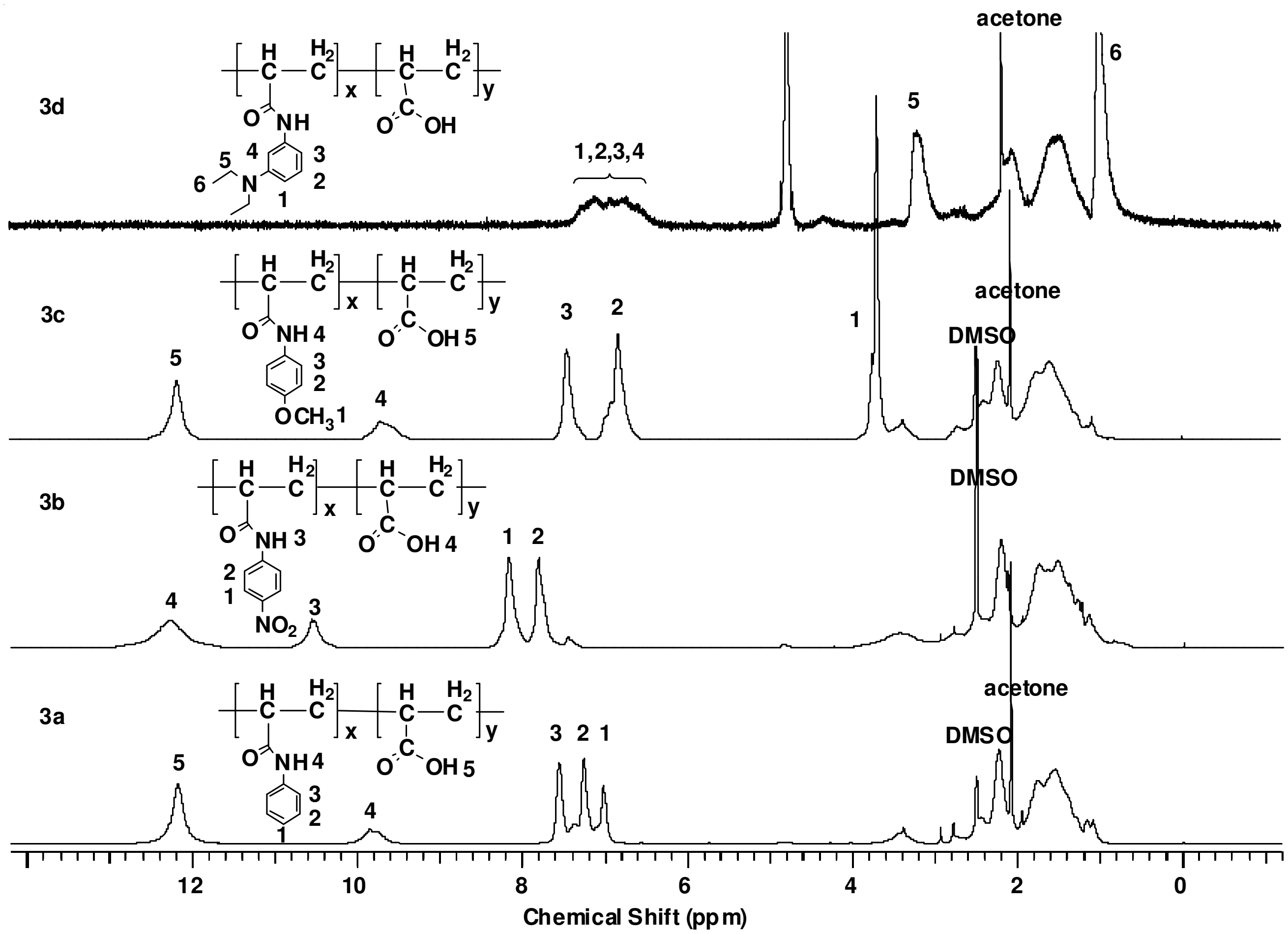


Fig. 2. ^{1}H NMR spectra of **3a-c** in DMSO-d_6 and **3d** in D_2O

TABLE-1
STRUCTURES, FUNCTIONALIZATION OF PAAn-*co*-AAc

P(AAm-AAc)	R_1	R_2	Molar ratio of aromatic amine to carboxyl group of poly(acrylic acid)	Functionalization[a] (%)	Aromatic amine conversion (%)
3a-1	H	H	1:4	24.1	96.4
3a-2	H	H	1:2	39.1	78.2
3a-3	H	H	1:1	52.7	52.7
3b-1	H	NO_2	1:4	23.8	95.2
3b-2	H	NO_2	1:2	37.4	74.8
3b-3	H	NO_2	1:1	46.7	46.7
3c-1	H	OCH_3	1:4	20.4	81.6
3c-2	H	OCH_3	1:2	34.3	68.6
3c-3	H	OCH_3	1:1	49.6	49.6
3d-1	$N(CH_2CH_3)_2$	H	1:4	24.0	96.0
3d-2	$N(CH_2CH_3)_2$	H	1:2	38.0	76.0
3d-3	$N(CH_2CH_3)_2$	H	1:1	46.6	46.6

[a]Content of aromatic units was calculated on the basis of determining the nitrogen content (N %) using the elemental analyses.

3-(N,N-diethylamino) (**1d**) substituted anilines were also used to investigate the amidation of poly(acrylic acid). As shown in Table-1, four kinds of aromatic amines with different substituentes can be used to effectively functionalize poly(acrylic acid) chain, which indicates this synthesis is a feasible method.

Conclusion

In this study, we have demonstrated a facile and efficient method for the synthesis of PAAn-*co*-AAc using the inexpensive thionyl chloride as an activating reagent. One of the most attractive advantages is that this strategy allows the synthesis of PAAn-*co*-AAc with poly(acrylic acid) and aromatic amines in one-pot without adding alkalis (such as triethylamine, pyridine, *etc*.). When the aromatic amine to poly(acrylic acid) (acrylic acid units) were added at a ratio of 1:1, the maximum F % of PAAn-*co*-AAc of the samples was obtained at 52.7 %. This strategy may furthermore afford the preparation of polyacrylanilides with different aromatic amines and potential application in the synthesis of other block copolymers containing acrylic acid or methylacrylic acid.

ACKNOWLEDGEMENTS

The authors are grateful to State Key Program of National Natural Science Foundation of China (20836001) and the National Key Technology R & D Program (2011BAE07B01).

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