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γ-Ray Irradiation Canal Polymerization Conditions Ensuring Highly Stereoregular (>80%) Poly(acrylonitrile)

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ABSTRACT: The optimum γ-ray irradiation canal polymerization conditions ensuring highly stereoregular poly(acrylonitrile) (PAN) were studied experimentally. That is, the characteristics of the canal polymerization in the solid state were briefly described. The preparation process consists of three elementary steps: (1) canal complex formation; (2) γ-ray irradiation; (3) recovery. The effect of experimental factors in each step on the stereoregularity of PAN was studied. Several essential factors were extracted, such as the mole ratio of AN to urea and aging time in step 1, the irradiation dose rate and temperature in step 2, and various recovery precautions in step 3. The extent of the stereoregularity of PAN obtained here was in the range 70–85%, and the highest value was 87% in triad units by ^{13}C NMR spectra. The optimum canal polymerization conditions producing high-quality stereoregular PAN samples with over 80% isotacticity in certain limited cases were disclosed experimentally.

Introduction

It is well-known that highly stereoregular poly(acrylonitrile) (PAN) can be prepared by γ-ray irradiation on an acrylonitrile– (AN) urea canal complex at a low temperature.[1] The PAN prepared by such a method has been proved to be essentially isotactic in its configuration.[2,3] There have already been several studies on the canal polymerization of AN,[4,5] but little significant information on the preparation of highly stereoregular PAN samples has been obtained.

Previously, one of us made a detailed experimental study of the γ-ray irradiated canal polymerization of AN.[6,7] The effect of canal polymerization conditions on the molecular weight and molecular weight distribution of the resulting polymer was reported. However, the effect of polymerization conditions on the stereoregularity of PAN was not studied at that time. In this paper, the problem is discussed in detail. Particular attention is paid to clarification of the sample preparation conditions, which ensure a highly stereoregular sample having more than 80% isotacticity. Previously reported values of the isotacticity of stereoregular PAN range from 50 to 70%,[8-13] and a value exceeding 80% has not been reported.

Recently, we made systematic experiments on the preparation of stereoregular PAN and could obtain a highly stereoregular sample whose isotacticity exceeds 80%. In some limited cases, an isotacticity of 87% was obtained, although its yield was quite low (<10%). These samples are expected to be effectively used for various research purposes such as the experimental confirmation of a fused-ring structure (i.e., an ideal intramolecular ring formation) in thermally oxidized PAN fibers, and the like. Here, the experimental conditions and other factors in obtaining such samples are briefly described.

Experimental Section

Sample Preparation. AN and urea were purified as described previously.[6,7] The complex was prepared by mixing AN with urea at a calculated mole ratio under vacuum, followed by cooling to a low temperature (−78 °C). All the samples were prepared by the γ-ray irradiation postpolymerization method.[14] Typical examples are shown in Table I.

^{13}C NMR Measurements. Besides the NMR spectrometers employed previously,[12] JEOL JNM GX-270, GSX-400, and GX-500 were used under similar conditions. The tacticity was determined based on the peak intensity of the methine (CH) carbon in the NMR spectra. The isotacticity defined here indicates the triad tacticity (based on three monomer units), and the percent isotacticity is the percentage of isotactic triad units to other configurational units. Pentad and heptad tacticity in several cases were briefly noted.

Infrared (IR) Measurements. Details of the IR measurements are given in ref 12.

Differential Scanning Calorimetry (DSC) Measurements. The complex formation process was traced by the DSC method. Besides the DSC instrument employed previously,[13] a MAC Science DSC apparatus was effectively used here. The

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Table I
Characterization of Some Selected Samples

					NMR results			
					triad tacticity[d]			
polymerizn[a]	run[b]	code	AN/urea mole ratio	PAN viscosity (η)[c]	I	H	S	$4IS/H^2$
canal	A	C-1	1/5	0.79	83	14	3	5.56
canal	A	C-2	1/3	0.99	80	15	5	6.54
canal	A	C-3	1/2.7	1.08	79	16	5	5.90
canal	B	C-4	1/7	1.52	84	13	3	6.75
canal	B	C-5	1/5	1.62	81	15	4	5.59
canal	B	C-7	1/2	3.05	69	23	8	4.13
canal	D	C-11	1/7	0.83	87	10	3	8.07
canal	D	C-12	1/5	1.12	84	13	3	6.69
canal		C-13	1/7	1.32	82	14	4	7.09
canal		C-15[e]	1/1	4.96	48	36	16	2.41
anionic		A-1[f]		2.26	31	46	23	1.41
radical		R-1[g]		0.61	29	49	22	1.10

[a] All the canal samples except C-15 were prepared by irradiation postpolymerization. The sample preparation conditions are given in Figure 8. Yield was relatively low (5–35%). [b] Symbols indicate the run number shown in Figure 8. [c] DMF, at 25 °C. [d] Peak intensity was calculated based on the methine (CH) carbon. [e] Used in a previous work.[12] [f] Prepared in THF by DSTBP, at −60 °C. [g] Prepared in isobutyraldehyde by AIBN, at 50 °C. Key: THF, tetrahydrofuran; DSTBP, 1,4-disodio-1,1,4,4-tetraphenylbutane; AIBN, azobisisobutyronitrile.

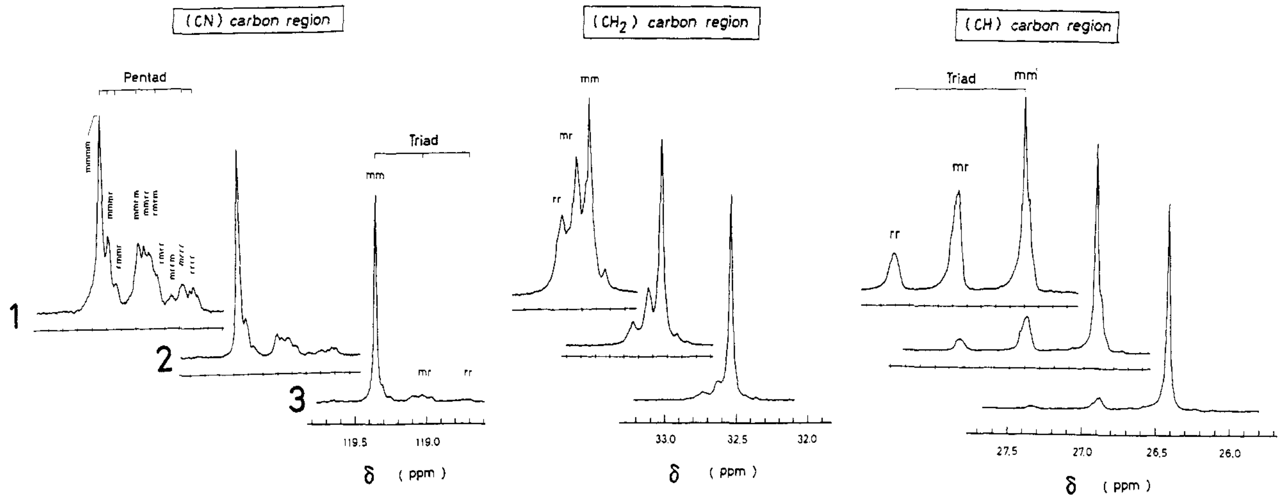


Figure 1. 100-MHz ^{13}C NMR spectra of several isotactic PAN. The notation given in ref 16 was used. Besides triad tacticity, pentad tacticity can be discussed. In the nitrile (CN) carbon, particularly, assignments can be given according to Balard[17] and Kamide,[10] as shown in sample 1 in Figure 1. Sample: 1, C-15, isotacticity, 48%; 2, C-7, 69%; 3, C-4, 84%.

DSC conditions were as follows: sample weight, 5–10 mg; heating rate, 20 °C/min; atmosphere, N_2.

Solubility Measurements. The dissolution temperature (T_{sol}) of PAN in *N,N*-dimethylformamide (DMF) was measured by use of laboratory-constructed laser-optical instruments (see ref 13).

Results and Discussion

Typical ^{13}C NMR Spectra of Highly Isotactic PAN. Typical ^{13}C NMR spectra of stereoregular PAN are shown in Figure 1. The difference in stereoregularity appears in the nitrile (CN) carbon and methine (CH) carbon in the NMR spectra.[2,3,15] In the former case, particularly, 10 peaks due to pentad tacticity are apparent and their assignments can be given as shown in Figure 1. It is possible to discuss the stereospecific polymerization mechanism of AN in the canal based on the NMR spectra, but this discussion is not made here.[18] The peak separation is not always clear for the methylene (CH_2) carbon in PAN.

In order to compare the extent of stereoregularity of PAN, previously reported experimental data are summarized in Figure 2. As emphasized by Kubasova et al.,[8] since the relative intensity of the isotactic and syndiotactic peaks (I/S) is a useful measure of stereoregularity of PAN, one can easily estimate the extent of stereoregularity of PAN by this figure. It is apparent that all the results lay on a smooth curve, and the results obtained here show quite high values of stereoregularity. When the results are plotted against the statistical index[19] defined by eq 1, Figure 3 is obtained

$$P = \frac{4IS}{H^2} \tag{1}$$

where the symbols I, S, and H indicate the peak intensities of isotactic, syndiotactic, and heterotactic configuration.

It is clearly seen that the experimental data lay on two straight lines with different slopes, and the difference of the slope in each line is probably closely related to the difference in polymerization mechanism: the insource polymerization and the postpolymerization. The exact reason why the results fit on two different lines is not clearly understood. However, it may be possible to consider that the main difference between them is the presence or absence of γ-ray bombardment during polymerization (see Figure 4). Chain scission caused by γ-ray bombardment may also play an important role in this case. That is, if chain scission occurs severely and fragmented chain ends permit free addition of AN monomer, the stereoregularity of the resulting polymer will decrease naturally. Such an effect will be reflected in the value of the statistical index (i.e., $4IS/H^2$) of the polymerization defined by eq 1. This effect, however, cannot be expected in the postpolymerization. In this

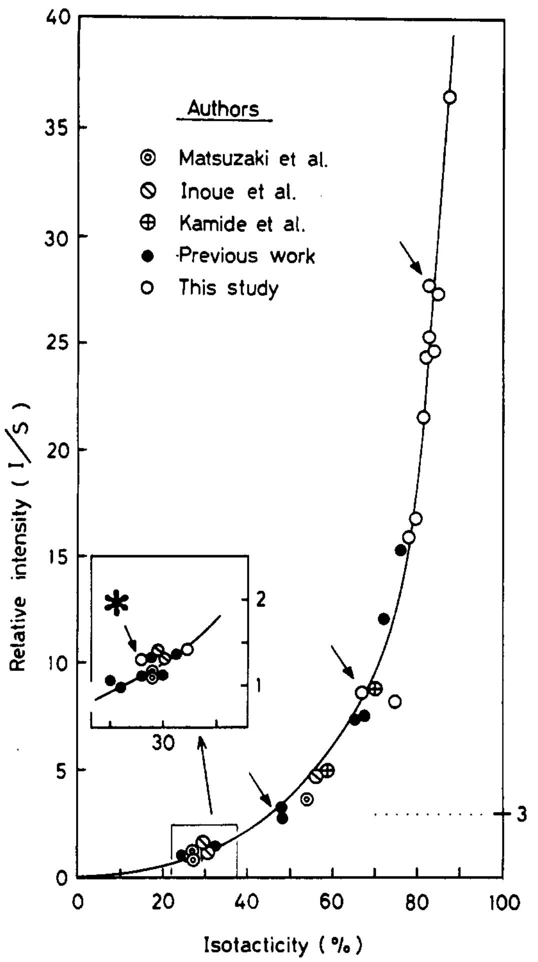


Figure 2. Summary of previously reported NMR results. The abscissa is the isotacticity (triad units) of PAN determined by ^{13}C NMR spectra. Kubasova[8] reported that the intensity ratio (I/S) of their sample is ca. 3. It is estimated that the isotacticity of their sample is about 50%. Much higher values are reported by Matsuzaki (54%), Inoue (56%), Kamide (70%), and us (76%). Samples having more than 80% isotacticity were reported here. Arrows indicate the samples used in Figure 1.

way, the difference in the slopes of two lines in Figure 3 is explained well, although it is merely an assumption and experimental confirmation is necessary.

The experimental data indicated by an asterisk are the results for PAN prepared by the free-radical method in an aldehyde medium (see Table I). This sample has been assigned a syndiotactic configuration based on X-ray analysis (density, IR, etc.) in connection with the improvement of regularity in PVC by aldehyde.[20] However, ^{13}C NMR results indicate that the sample is essentially an atactic configuration. That is, the relative intensity of the NMR peak (I:H:S) was 2:5:3, which suggests that the tacticity is essentially atactic. As for the stereoregularity of PAN, there is considerable confusion (e.g., syndiotactic,[20,21] syndiotactic rich,[22,23] and atactic[2,24]) but ^{13}C NMR spectroscopy revealed that ordinary free-radical PAN is essentially atactic and canal-polymerized PAN is isotactic.[2,3,15] With regard to anionic PAN, two different results have been reported: i.e., atactic[3,15] and isotactic.[25] In the latter case, particularly, the extent of isotacticity ranged from 30 to 59% according to the preparation conditions. However, we could not obtain such stereoregular samples by the anionic method within our own experimental range (see Table I).

Characteristics of γ-Ray Polymerization in the Solid State. The canal polymerization consists of three elementary steps: (I) complex formation, (II) γ-ray irradiation, and (III) recovery (see Figure 4, left). Urea itself has a tetragonal lattice structure, but in the presence of lower organic substances including AN, it causes a crystalline transformation and the hexagonal lattice of urea, with AN in the central position, is formed (Figure 5). This process can be traced by DSC measurements (Figure 6). That is, when the complex is formed, the melting peak of AN (−75.5 °C) disappears and a new endothermic peak due to the decomposition of the canal complex appears at a higher temperature (−20.8 °C).[30] A similar endothermic peak due to the decomposition of the canal for other monomers has been studied by many authors.[31] At any rate, one can estimate the extent of the aging of the canal complex in the bulk state. When DSC measurements are made for an AN/urea mixture, Figure 11 is obtained (see a later section). This figure, a kind of phase diagram, indicates the larger the mole ratio, the longer the aging time. This figure also can be effectively used for a discussion of the optimum canal polymerization conditions ensuring high-quality stereoregular PAN samples, as described later.

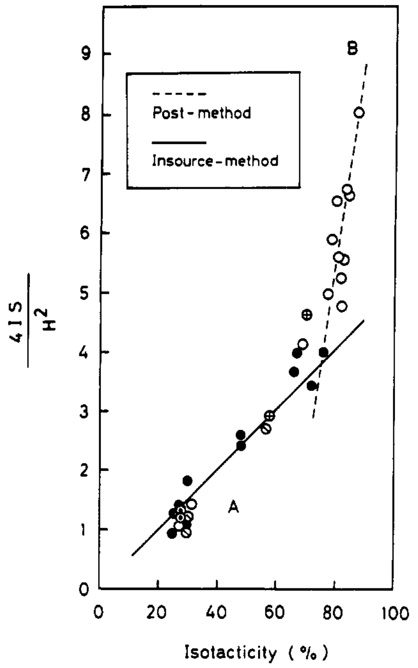


Figure 3. Relation between statistical index ($4IS/H^2$) and isotacticity of PAN. The meaning of symbols in Figure 3 is the same as in Figure 2. Although the details of sample preparation are not always described in refs 2, 3, and 10, it appears to be true that these samples are prepared by the insource method. As a matter of fact, these data fit on straight line A rather than line B.

As for the γ-ray irradiation, there are two different types of procedures: (i) the insource polymerization and (ii) the radiation postpolymerization (see Figure 4, left). In the former case, the canal complex prepared at dry ice/methanol temperature (−78 °C) is directly irradiated at this temperature. This is the most general canal polymerization, and the polymerization proceeds under the bombardment of γ-ray irradiation. In the latter case, however, the prepared canal complex is cooled to a much lower temperature, i.e., liquid nitrogen temperature (−196 °C), and γ-rays are irradiated. The polymerization does not take place at liquid N_2 temperature, but it does when the temperature is raised above −100 °C. Therefore, one can separate the γ-ray irradiation step and the polymerization step. The polymerization proceeds without γ-ray irradiation, and the damage to the resulting polymer by irradiation can be prevented. Although stereoregular

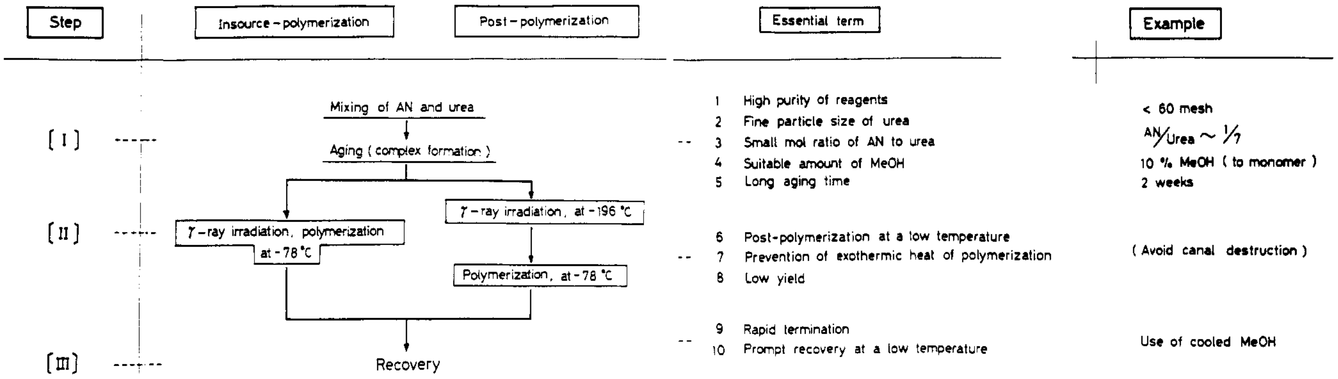


Figure 4. Flow sheet and several significant factors in the preparation of high-quality isotactic PAN.

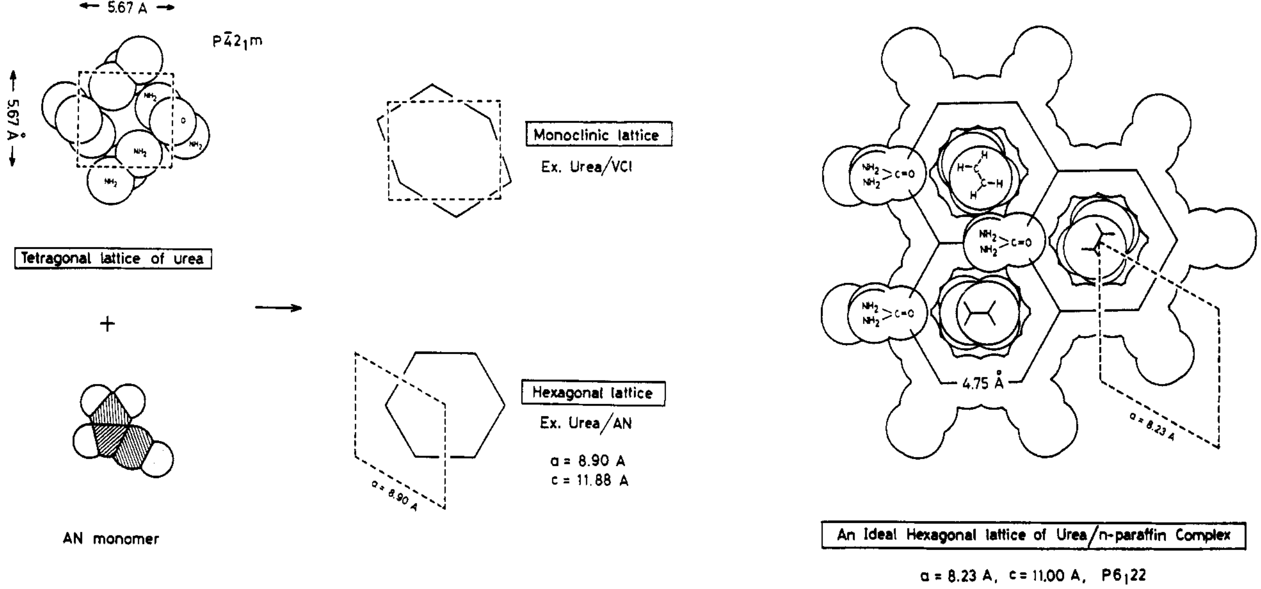


Figure 5. Structural change in the complex formation process. It must be noted that the complex is by no means formed after the complete formation of a hexagonal lattice of urea, with the AN oriented in the canal. The complex is formed simultaneously through the crystalline transformation and the involvement of AN in the central position. The structure of the canal complex varies according to the difference of the kinds of monomers.[26,27] An ideal hexagonal lattice is attained only in *n*-paraffin/urea complex, etc.[28,29] Monoclinic and orthorhombic structures are formed in vinyl chloride (VCl) and butadiene, respectively.[26,27] In the case of AN, a pseudohexagonal lattice having a dimension of 8.90 Å (*a*-, *b*-axes) has been reported tentatively,[30] although strict X-ray structural analysis in this case is quite difficult due to the fact that an ideal single crystal of the canal complex (i.e., needlelike complex) cannot be obtained.

PAN can be prepared by both methods, it was expected that the latter method would ensure better stereoregularity of PAN due to a lack of high-energy radiation during polymerization. In fact, all the samples obtained here were prepared by the latter method (i.e., the postpolymerization method). (See Figure 3.)

Further, it must be noted that, in the canal polymerization of AN, the destruction of the canal invariably occurs with the progress of polymerization.[30] Such unique behavior of various monomers with urea canal complexes has been studied by many authors.[26,31] In the case of AN, it can be detected by broad-line (^1H) NMR measurements (Figure 7). The key point of this experiment is the use of deuteriated urea (urea-d_4) in complex formation. That is, when γ-rays are irradiated, a sharp resonance line appears, overlapping that of the broad component in the NMR spectra. The former has been assigned to be the proton in free AN liberated and the latter the proton in the complex forming AN.[30] Destruction of the canal is probably induced by (1) the dimensional change of guest molecules (AN → PAN) and partly by (2) the local temperature elevation by the heat of polymerization. The effect of the latter (2) is relatively strong, and this deteriorative effect cannot be overlooked so as to obtain a high-quality stereoregular PAN sample.

Stereoregularity of PAN and Canal Polymerization Factors. (I) Effect of Complex Formation Factors. The primary factor is the mole ratio of AN to urea. Generally, the smaller the mole ratio, the higher the stereoregularity of PAN. This is shown typically in Figure 8. The difference in the slope and absolute value of the tacticity of each line is caused by other factors such as the extent of aging of the canal complex, etc. Higher values are obtained when the complex is formed adequately (see a later section).

The second important factor is the aging factor in relation to the presence of methanol. That is, as has been observed by White,[1] a small amount of methanol acts as a nucleation agent (or an accelerator) in complex formation. In the absence of methanol, it takes about 18 days for AN to complete the urea canal complex formation. In the presence of methanol, it takes only 8 days.[1] According to our results, however, aging time depends strongly on actually employed factors such as mole ratio of AN to urea, etc. The preparation of urea, its particle size, and the amount of methanol are all closely related to this problem. That is, if the results reported by White are true, NMR spectra of PAN measured as a function of aging time will show some drastic change in certain aging times. But, in our experiments, such results were not

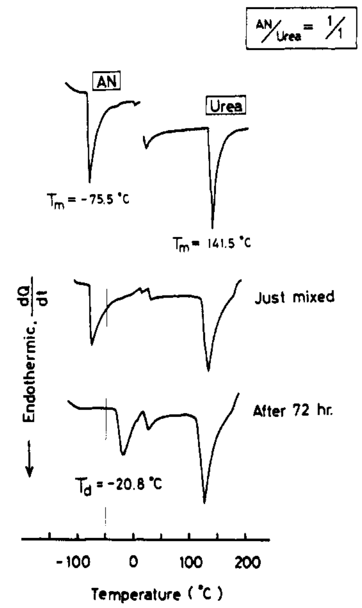
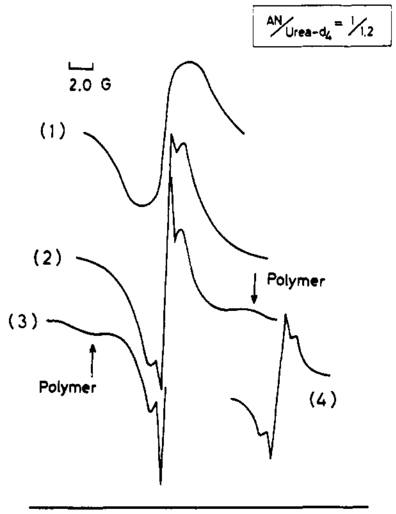


Figure 6. DSC traces in the complex formation process. In the DSC curve of the canal complex, an endothermic peak due to the decomposition of the complex is observed.[31] The appearance of T_d with the simultaneous disappearance of T_m of AN is a useful measure of the extent of the aging of the canal complex. A phase diagram in Figure 11 was obtained in this way.



Taken from ref. 30

Figure 7. Change in ^{1}H NMR spectra during γ-ray irradiation. When γ-rays were irradiated, a sharp resonance line appears overlapping on a broad component. The results can be reasonably explained in terms of the destruction of the canal complex: liberation of free AN.[30] The amount of free AN increased, when the temperature was increased. The temperature was increased stepwise. Conditions: 1, before irradiation, -90 °C; 2, after irradiation, -90 °C; 3, -70 °C; 4, -5 °C.

obtained. As shown in Figure 9, it is apparent that the stereoregularity of PAN was quite high (~75%) and was almost constant under the given conditions. In other words, complex formation was completed within a few days under the conditions given in Figure 9. It is possible to say that an aging time of 1–2 weeks was adequate to obtain good results.

(II) Effect of γ-Ray Irradiation Factors. The effect of polymerization temperature was studied. NMR spectra are shown in Figure 10. Several related results are summarized in Table II. NMR results show that stereoregularity decreases when the polymerization temperature is increased. The results can be explained in terms

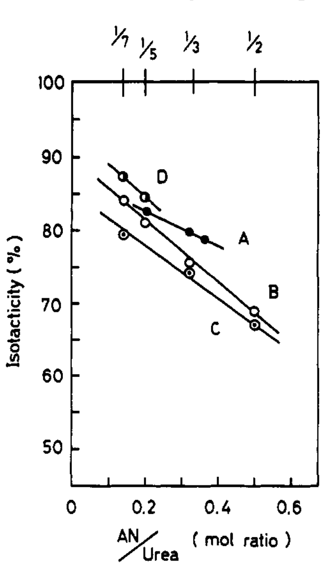


Figure 8. Effect of mole ratio (AN/urea) in the complex formation step on stereoregularity of PAN. The samples were prepared under different composition range (AN/urea = 1/2–1/7). Attention was paid to every step in the sample preparation, as described in the text. Symbols A–D indicate different experimental runs (see Table I). Conditions: method, postpolymerization; mole ratio (AN/urea), 1/7–1/2; aging time, 1–2 weeks; irradiation conditions, 0.5 Mrad/h × 2–3 h, at -196 °C (or 1 Mrad/h × 2–3 h, at -196 °C).

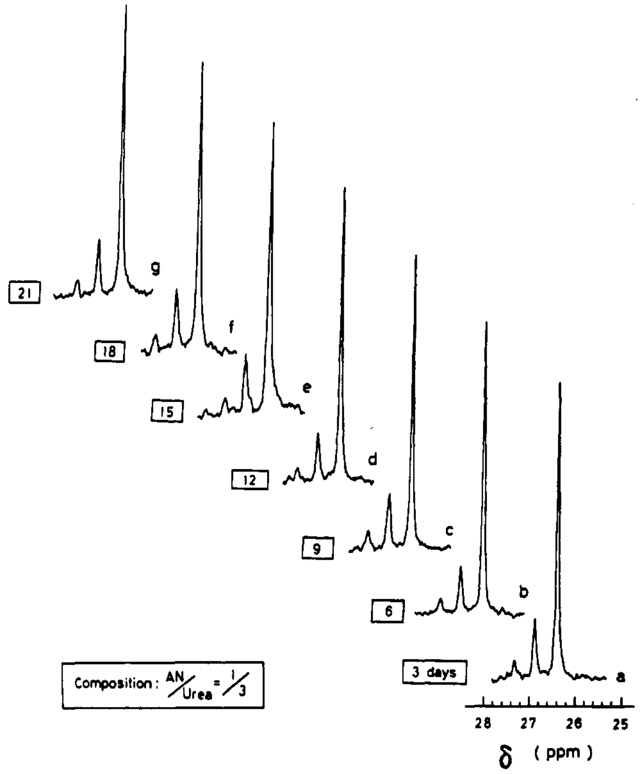


Figure 9. Effect of aging time in the complex formation step on NMR results of PAN. NMR spectra were taken for the samples prepared with different aging times. The isotacticity (a–g) was almost constant: 75%, 75%, 72%, 75%, 71%, 75%, and 74%, respectively. The sample preparation conditions are given in Figure 8.

of the stability of the canal complex. That is to say, the urea canal complex of AN is relatively stable only at a low temperature. When the temperature is increased, the complex becomes unstable and in some cases is destroyed. Therefore, at an increased temperature, (a) a perfect canal, (b) an imperfect canal, and (c) a destroyed one (i.e., a simple mixture of AN and urea) are formed. Although

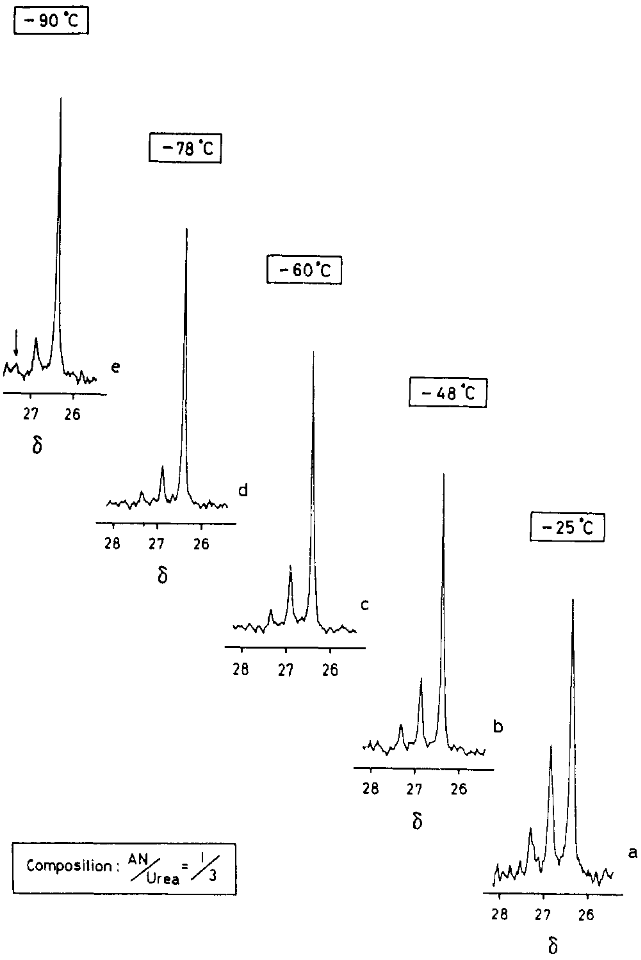


Figure 10. Effect of polymerization temperature on NMR results. The samples were prepared under the same conditions given in Figure 8 except with different polymerization temperatures. The isotacticity increased from 56 to 81% when the temperature was decreased.

Table II
Effect of Polymerization Temperature on Stereoregularity and Related Properties of PAN

polym temp[a] (°C)	yield (%)	PAN viscosity $(\eta)^b$	NMR isotacticity (%)	dissolution T_{sol} (°C)	IR D_{1230}/D_{1250}[c]
-90	3	1.75	81	135	*d*
-78	24	1.77	78	131	0.61
-60	40	2.61	72	125	0.58
-48	45	2.96	68	115	0.55
-25	61	3.75	56	107	0.51

[a] The complex with the composition AN/urea = 1/3 was irradiated (1 Mrad/h × 2 h) at liquid N_2 temperature and then maintained at each temperature. [b] DMF, at 25 °C. [c] Intensity ratio of absorbance of the IR characteristic bands.[12] [d] Calculation was impossible due to the overlapping of a broad IR band of impurity; i.e., fine pieces of Pyrex glass tube were included in the sample, when an ampule was broken at a low temperature.

the relative composition of these components will depend on the temperature, it is sure that the content of the perfect canal decreases when the temperature is increased. Since an ideal isotactic configuration can be attained only within the perfect canal, the decrease of stereoregularity with an increased temperature is quite natural in this case. Since destruction of the canal is also accelerated by the quite local temperature elevation due to the heat of polymerization, it is by all means necessary to control the experimental factor of heat or temperature.

The effect of irradiation dose rate must be noted. In general, weak irradiation dose (or small dose rate) was advantageous in the insource experiments. In the case of the postpolymerization, however, this appears not to be true. In one example, the dose rate of (0.5 Mrad/h × 2 h) on the complex with the mole ratio of 1/3 (AN/urea) ensured 80% isotacticity, and the dose rate of (1 Mrad/h × 2 h) ensured 82% isotacticity under the same conditions. There was very little difference in the results of the irradiation dose rate on the regularity of PAN. Since the problem of dose rate appears to be related to the extent of the destruction of the canal complex, further detailed studies must be made in this respect.

(III) Effect of Recovery Procedure. It must be noted that, in the canal polymerization, the process is only terminated by adding methanol or bline water, since polymerization in the solid state proceeds like living polymerization. One can confirm the progress of polymerization at room temperature. That is, when the reaction vessel was taken from a dry ice/methanol bath and brought to room temperature, its temperature increased rapidly. In order to prevent the progress of polymerization at room temperature, the use of cooled methanol and a prompt recovery, etc., are essential. This is particularly true for obtaining a high-quality stereoregular PAN sample with over 80% isotacticity.

Optimum Polymerization Conditions Ensuring 80% Isotacticity. From the above results, one can extract several essential terms. These are summarized in Figure 4 (right). We have not yet succeeded in preparation of a completely stereoregular PAN (isotacticity being 100%), but it is sure that these factors are undoubtedly important factors in obtaining such samples as a goal.

The significance of the optimum conditions ensuring such results must be noted (see Figure 11). Two straight lines (U and V) are drawn overlapping on a phase diagram. Line V ensures 75% isotacticity, and the extent of the regularity on this line is almost constant (see Figure 9). Much higher regularity is attained on line U. When the mole ratio is decreased, the stereoregularity increases gradually. In the optimum region (AN/urea ~ 1/7), the regularity over 80% isotacticity is realized constantly. This is exemplified in Figure 8 (and Table I). It is worthwhile noting that Figure 8 is a clear cut of the NMR results along line U.

The advantageousness in the postpolymerization for the preparation of a high-quality sample also should be noted. This is clearly indicated by the difference in the slope of two lines in Figure 3. That is, as stated above, the most significant difference in the two kinds of polymerization methods is the presence or absence of γ-ray bombardment during polymerization. In the postpolymerization method, the net propagation reaction will be attained by pure translational molecular motion of AN in the canal. In the insource method, if chain fragmentation caused by γ-ray bombardment occurs severly, the addition of AN monomer will occur not only in the oriented canal but also in the destroyed one. Such a deteriorative effect will cause the decrease of stereoregularity of the bulk sample. In order to obtain a high-quality sample, therefore, canal conditions must be selected carefully.

^{13}C NMR spectra (125 MHz) of high-quality stereoregular PAN sample are shown in Figure 12. A recent monograph describes the theoretical prediction of pentad and heptad tacticity of vinyl polymers.[32] Figure 12 indicates that the heptad tacticity of PAN agrees well with this theoretical prediction. That is, in the comparison of the NMR spectra between anionic- and isotactic-samples, the main peak at 119.32 ppm can be correlated with heptad tacticity of PAN. That is, pentad tacticity

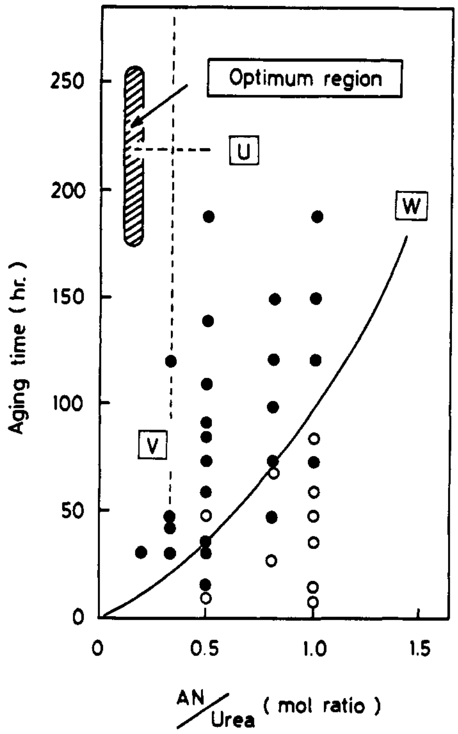


Figure 11. Aging map as a function of mole ratio of AN to urea and optimum region. Curve W indicates the transition zone, below which no complex is formed and above which the complex is formed substantially. The structural change of urea from tetragonal to hexagonal lattice before and after complex formation has been discussed based on the WAXD pattern in ref 6. Results for the samples prepared along lines U and V are shown in Figures 8 and 9, respectively. High-quality PAN samples with over 80% isotacticity were obtained under the optimum region indicated in this figure. Further, a much smaller mole ratio did not always produce good regularity of PAN. That is, when the mole ratio was smaller (1/10, 1/15, 1/20), the isotacticity rather decreased (75%, 73%, 73%).

(mmmm) in Figure 1 is clearly separated in heptad tacticity (mmmmmm, rmmmmm, rmmmmr) in Figure 12, as described in ref 32, and the main peak of isotactic PAN agrees with the third one.[33] It is likely that highly stereoregular PAN obtained here consists of almost completely rmmmmr sequence alone, since no other tactic peaks were observed.

Conclusion

The γ-ray irradiation canal polymerization conditions ensuring highly stereoregular PAN were studied in detail. The characteristics of the polymerization in the solid state were briefly described. The preparation process consists of three elementary steps, and the effect of each factor in these steps on the stereoregularity of PAN was studied. Particularly important physicochemical factors were extracted. The optimum canal conditions ensuring more than 80% isotacticity of PAN were disclosed in some limited cases. NMR spectroscopic information on highly isotactic PAN was briefly described.

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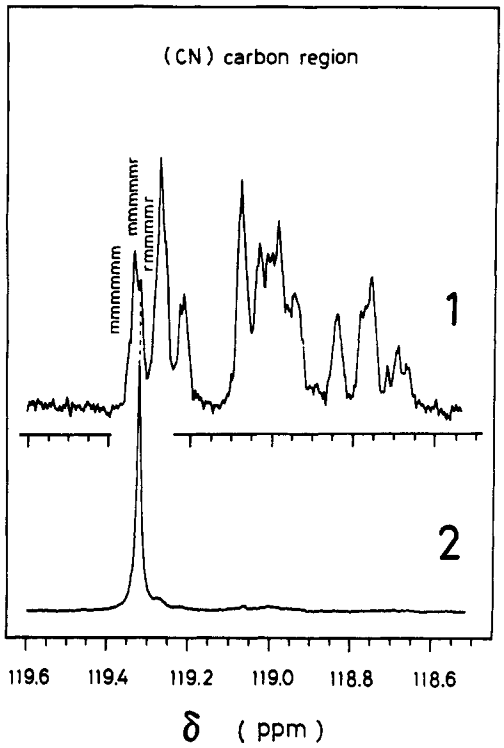

Figure 12. Assignment of heptad tacticity in the CN carbon region of PAN based on 125-MHz ^{13}C NMR spectra. Sample: 1, anionic, A-1, 31%; 2, canal, C-11, 87%.

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Registry No. PAN (homopolymer), 25014-41-9; AN, 107-13-1; H_2NCONH_2, 57-13-6.