

Kinetics and Statistics of Structural Changes in Polyacrylonitrile

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폴리아크릴로니트릴의 構造變化에 있어서의 動力學的 및 統計學的 研究

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要 約

폴리아크릴로니트릴을 加熱할 때 着色과 同時에 構造變化가 있다는 것은 잘 알려진 事實이며 이것은 部分 水素화나프틸리딘型環을 形成함에 基因하는 것으로 알려지고 있다. 本研究는 이와 같은 構造變化의 反應을 動力學的 및 統計學的으로 取扱하여 지금까지 알려지지 않았던 새로운 事實들을 發見하였다.

첫째로 폴리아크릴로니트릴을 加熱할 때의 니트릴基의 減少는 一次反應이라는 것이며 이는 環形成反應이 긴 連鎖反應으로 이루어지지 않는다는 것을 말해 주는 것이다. 다시 말하면 環形成時의 kinetic chain length는 極히 짧다는 것이다. 또 本 構造變化는 반드시 分子間反應(架橋結合)이 아니더라도 일어날 수 있다는 것을 證明했다.

둘째로 環形成으로 니트릴基가 減少할 때 19~22%의 니트릴基가 殘存한다는 것이며 이를 統計學的으로 解析해본 結果 19.2%라는 計算值을 얻었으며 이는 實驗值과 잘 맞는 數值이다.

Abstract

It is well known that the coloration and structural changes in thermal treatment of polyacrylonitrile are due to the formation of partly hydrogenated naphthylidene-type ring involving the pendant nitrile groups. Any quantitative study of the reaction, in the sense of kinetics and/or statistics, however, has never been reported.

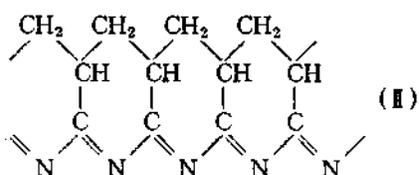
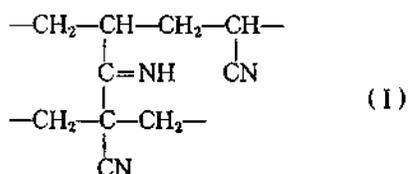
This paper presents that, at first, the disappearance of the nitrile groups follows the first order kinetics, which indicates clearly that nitrile groups do not disappear by a long chain reaction—the kinetic chain length is very short. This observation rules out the long intramolecular and intermolecular propagation chain through which most of the nitrile groups disappear. From the evidence that a similar reaction occurs in propylene carbonate solutions without gel formation, one may conclude that the coloration and structural changes are not necessarily intermolecular reaction. Secondly, a finite amount of nitrile groups remains unreacted at the extrem of reaction—not contributed to the formation of naphthylidene-type ring.

The concentration of this unreacted nitrile groups is 19~22% which is in good agreement with the statistically calculated value of 19.2%.

INTRODUCTION

Since Houtz⁽¹⁾ proposed the formation of substituted pyridines, naphthylidines and higher condensed systems to adequately explain the coloration and insolubilization of thermally treated polyacrylonitrile, many papers⁽²⁾⁻⁽¹⁴⁾ have been published to discuss those phenomena. Schurz and his co-workers⁽⁶⁾ pointed out that the naphthylidine-type ring structure is a quite hypothetical, and attacked this mechanism on the basis of the fact that the physical properties of the thermally treated polymer, particularly, the spectral characteristics do not agree with the naphthylidine-type ring structure. The postulated reaction scheme by them involved the formation of azomethine-type intermolecularly crosslinked structure by condensation of a nitrile group from an adjacent chain with a tertiary hydrogen of the polymer chain. However, Grassie and his co-workers⁽¹³⁾ suggested that the formation of an intramolecular ring structure which initiated the formation of partly hydrogenated naphthylidine-type structure. Infrared analysis supported the change from nitrile to substituted imine and polyimine structure.

In the coloration of polyacrylonitrile by alkali, Schurz et al⁽¹¹⁾ suggested that the formation of intermolecular crosslinking like secondary amide bridge(I), while Grassie⁽⁷⁾ proposed the formation of partly hydrogenated naphthylidine-type structure(II), which was initiated by nucleophilic reagents.



The results, investigating the heat and alkali coloration of polyacrylonitrile with model compounds by Takada et al⁽¹⁴⁾, also supported Grassie's proposal.

In spite of many qualitative observations and the fact that analogies with more carefully studied reactions suggest quite plausible mechanism for this reaction, a quantitative study of the reaction has been absent in the body of literature concerning this reaction. This paper presents the study of the naphthylidine-type ring formation kinetics and statistics, consistent with the reported chemistry of reaction.

EXPERIMENTAL

<Monomer>

Commercial acrylonitrile(J. T. Baker Chem. Co) was purified by washing twice with 20% caustic soda solution and several times with distilled water, and then dried over calcium chloride. This treatment gave monomer of standard purity as described by Grassie.⁽¹³⁾ This monomer was degassed and distilled in a high vacuum line before use.

<Initiator>

Azobisisobutyronitrile(Monomer-Polymer Lab., The Borden Chem. Co.), recrystallized from ethanol and then dried in vacuo.

<Preparation of Polymer>

Monomer was degassed by two or three freeze-thaw cycles and twice distilled in a high vacuum line similar to that described by Morton⁽¹⁵⁾ into Pyrex tube containing approximately 1% initiator. This tube was finally sealed under vacuum. The polymerization were carried out in a thermostat at 40°C for 30 minutes. Polyacrylonitrile, which was insoluble in monomer and precipitated during polymerization, was washed with methanol and dried under vacuum at room temperature for several days. No attempt was made to purify by reprecipitation, since a good solvent for polyacrylonitrile, dimethylformamide, was found to be efficient coloration-initiating agent.⁽¹³⁾

Intrinsic viscosity was determined in dimeth-

ylformamide solution at 30°C in a Cannon-Ubbelohde viscometer. The number average molecular weight of the polymer was 600,000 calculating from the following equation.

$$[\eta] = 3.92 \times 10^{-4} M_n^{0.75} \quad (16)$$

<Heat Treatment of Polyacrylonitrile>

0.2~0.3g of finely divided polymer samples were placed in Pyrex glass tubes (OD 12mm), which were sealed under high vacuum (2-3 μ Hg). Heat treatment of polyacrylonitrile were carried out in the preheated furnace for various time intervals. A 15 min. period was used to heat up the sample from room temperature to 200°C. Fluctuation of the final temperature was $\pm 0.2^\circ\text{C}$. After the heat-treatment of polymers, the samples were made into KBr discs. In following the changes in the infrared spectrum which occur during coloration, KBr disc technique carrying out the reaction in the disc described by Grassie⁽¹³⁾ was tried. This technique could not be used since considerable amount of scattering of the infrared beam developed during heat-treatment under a high vacuum.

<Infrared Spectra and Determination of Nitrile>

The heat-treated and untreated polymers were ground and incorporated into potassium bromide discs (6mg \pm 0.05mg of polymer/1.2g \pm 0.2mg of potassium bromide) and measured on a Perkin-Elmer model 221 double-beam infrared spectrophotometer with a sodium chloride prism. The thickness of potassium bromide discs were 33 \pm

0.2 mils. Preliminary test indicated that the tolerance of thickness were within the limit of reproducibility of the instrument.

The relative concentration of nitrile groups with respect to time was determined from the infrared absorption peak at 2237 cm^{-1} which is assigned to the $-\text{C}\equiv\text{N}$. Thermally untreated polyacrylonitrile at different concentration in potassium bromide was used for the calibration of nitrile concentration in the polymer. The linearity between the $-\text{C}\equiv\text{N}$ absorption and the concentration was observed as shown in Fig. 1.

RESULTS AND DISCUSSION

A. Ring Formation Kinetics; Preliminary test showed that some degradation of polyacrylonitrile occurs rapidly on heating the sample above 250~260°C or higher^{(18), (20)} as reported by Grassie⁽¹³⁾ and Straus⁽¹⁷⁾, while at the temperature up to 220°C no volatile products observed. All experiments described in this paper were carried out at temperature up to 220°C, therefore, the results are not attributed to any reaction involving loss of volatile materials.

During the heat-treatment of polyacrylonitrile, light yellow or yellow color developed even at 220°C for 72 hours, but not deep color (e. g. red orange-red-dark red) as reported before, while the heat-treated polyacrylonitrile discolored deeply if the vacuum of sealed tube was not enough. This means that oxygen accelerated the coloration of polyacrylonitrile.

The spectra of thermally treated polyacrylonitrile were similar to those reported before^{(2), (13), (14), (18)} in which the nitrile absorption peak decreased and the absorption at 1670 cm^{-1} and 1590 cm^{-1} region which might be arised from the conjugated carbon-nitrogen bond increased in intensity. The disappearance of nitrile groups with time at 170°C, 200°C and 220°C respectively, is graphically shown in Fig. 2. As illustrated in Fig. 2, a finite amount of nitrile groups remains

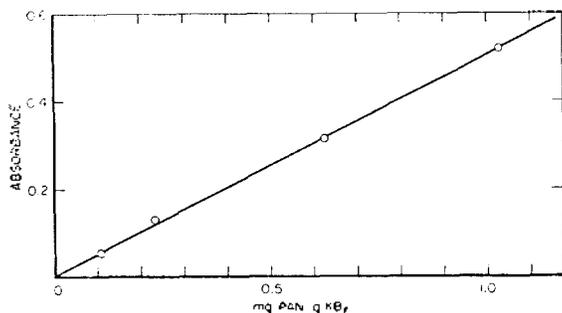


Fig. 1 Linear Relationship between the Concentration of Polyacrylonitrile in KBr disc and absorbance in 2237 cm^{-1} .

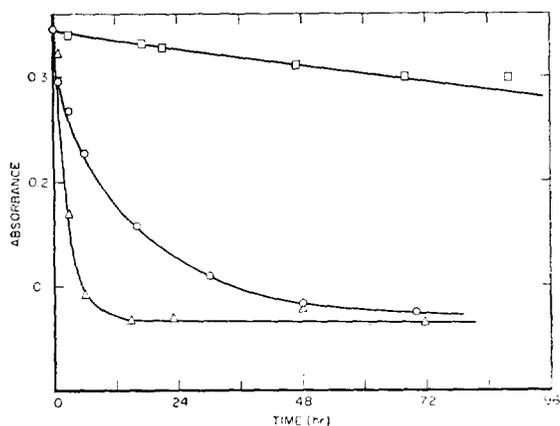


Fig. 2 The disappearance of nitrile groups with time.
 □; 170°C ○; 200°C △; 220°C

unreacted under such condition that the samples were heated even at 220°C for 72 hours. The

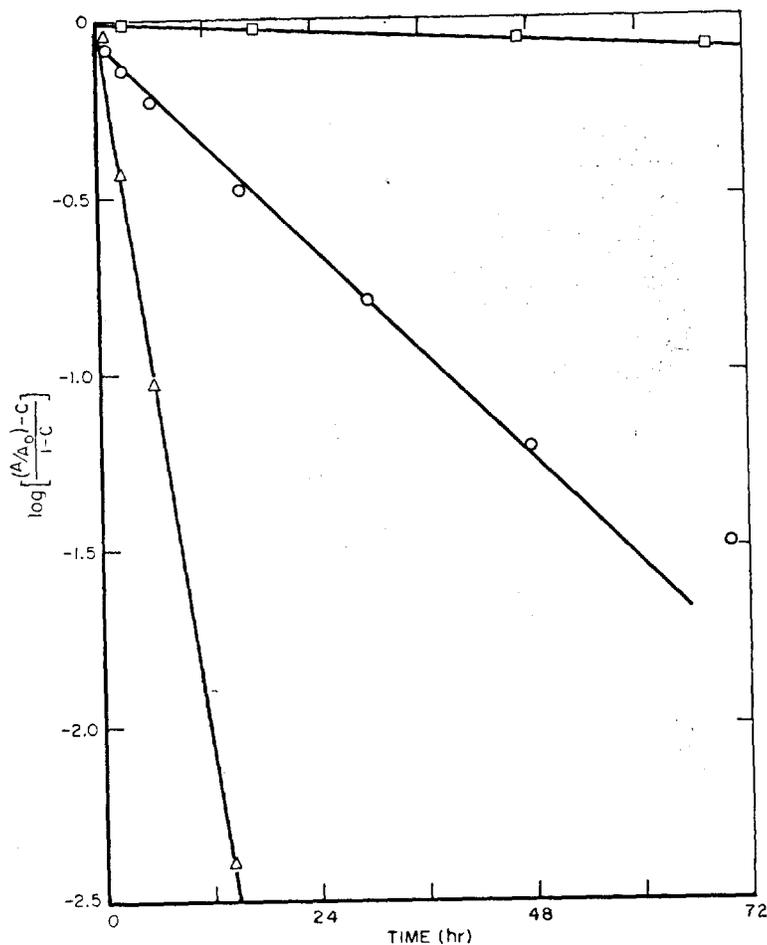


Fig. 3 The first order decay of the reactive nitrile groups.
 □; 170°C, ○; 200°C, △ 220°C

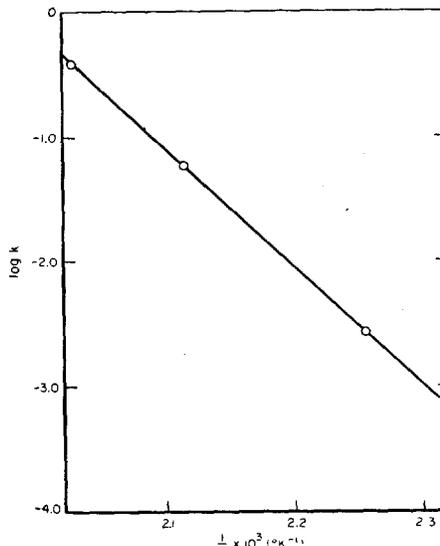
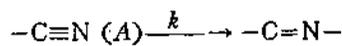


Fig. 4 Arrhenius plot.

residual relative concentration of the nitrile groups was 19~22% with slight variation with temperature within this range. This fact that a finite amount of nitrile groups remains unreacted will be discussed later.

Supposing that all of the nitrile groups were converted to conjugated $-C=N-$, and the reaction were to be first order, this reaction could be considered as follows:



$$-\frac{dA}{dt} = kA$$

$$-\frac{d(1-C)A}{dt} = k(1-C)A$$

Integrating this equation, yields

$$A = (1-C)A_0 e^{-kt} + CA_0$$

Where A_0 is the initial concentration of nitrile groups and the constant C is the fraction of the unreacted nitrile groups

in the asymptotic limit,

$$\frac{A}{A_0} = (1-C)e^{-kt} + C \text{ or } \ln\left(\frac{(A/A_0)-C}{1-C}\right) = -kt$$

A/A_0 can be expressed as a ratio of absorbance of $-C\equiv N$ peak in untreated polyacrylonitrile to that in thermally treated polyacrylonitrile. It is apparent that plots of $\log\left(\frac{(A/A_0)-C}{1-C}\right)$ vs. time will give straight lines with slopes of $-k$. The first order decay of the reactive nitrile groups is best illustrated in Fig. 3 and Fig. 4 shows the Arrhenius plot. The first order rate constant is readily obtained and

$$k = 1.5 \times 10^{15} e^{-43000/RT} \text{ (sec}^{-1}\text{)}$$

the activation energy of the formation of naphthylidene-type ring is 43 Kcal/mole.

Two main points are to be made from the observations—(1) The disappearance of the nitrile groups follows the first order kinetics. (2) A finite amount of the nitrile groups remains unreacted.

The first order kinetics indicates clearly that nitrile groups do not disappear by a long chain reaction—the kinetic chain length is very short. This observation essentially rules out the long intramolecular and intermolecular propagation chain through which most of the nitrile groups disappear.

It is of interest to note in this connection

that the structural changes are not necessarily intermolecular reactions either in the initiation or in the propagation⁽¹³⁾—so called “propagation crosslink”—because it was able to induce the same changes in the polyacrylonitrile in propylene carbonate solutions without gel formation. The concentration of polyacrylonitrile in propylene carbonate were 1 g PAN/ml PC and 0.1 g PAN/ml PC, and the thermal treatments were carried out in the vacuum-sealed tube at 200°C for 3 hours. On the other hand, by Grassie, in the heat-treatment of polyacrylonitrile in bulk at 200°C for 1 hour insolubility developed above 90%.

B. Statistical Consideration in Naphthylidene-type Ring Formation ; The second point of this study that a finite amount of the nitrile groups remains unreacted can be well interpreted by a statistical consideration of the proposed initiation reaction which is the intramolecular ring closure mechanism of the initiation to propagate to the partly hydrogenated naphthylidene structure. The formation of a six-membered ring which involved five carbon atoms in polymer backbone and one nitrile carbon atom has postulated⁽¹³⁾ as the initiation step from which the hydrogenated naphthylidene-type structure is

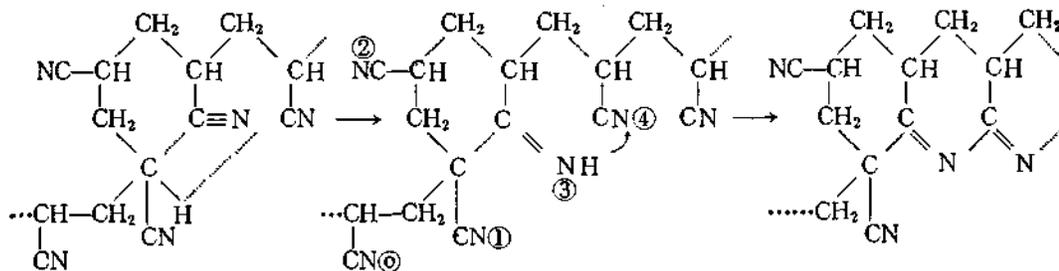


Fig. 5

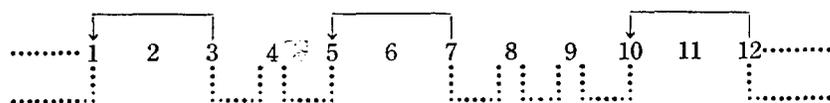


Fig. 6

propagated as in Fig. 5.

By numbering the pendant nitrile groups further along a polymer chain, the initiation and the propagation step can be represented schematically at the completion of the reaction as in Fig. 6, where the solid lines show the initiation ring and the dotted lines the propagation ring of the naphthylidene-type. The nitrile groups numbered 3, 7 and 12 are destroyed in the initiation step (as in Fig. 5) and the terminal groups of the step numbered 1, 5 and 10 will disappear by the subsequent short propagation step. It is apparent that the resulting chemical structure of a polymer chain leaves one nitrile group (2, 6 and 11) unreacted per initiation step which can not participate in the propagation.

Consequently the problem of the unreacted nitrile groups reduces to the calculation of the most probable number of the initiation rings m , given the total number of nitrile groups n in a polymer chain. This is possible only if the first order kinetics is the necessary and sufficient condition for a short kinetic chain length which is independent of time. It can be clarified with the following argument.

Let us consider the crystallization of one dimensional amorphous phase. The nucleation process can be regarded as the initiation step of six-membered ring formation, and the crystal growth as the propagation step. The crystallization kinetics is expressed by

$$1 - X(t) = \exp \left\{ - \int_0^t 2G(t-\tau)I d\tau \right\} \quad (1)$$

where $X(t)$ is the degree of crystallinity at time t , G the growth rate and I the nucleation rate. Under steady-state conditions eq. (1) reduces to

$$1 - X(t) = \exp \{-GI t^2\} \quad (2)$$

This is not a first order equation. A simple first order decay of the amorphous phase will result only when the growth length $2G(t-\tau)$ in eq. (1) is independent of time, and the corresponding equation is

$$1 - X(t) = \exp \{-\langle b \rangle I t\} \quad (3)$$

where $\langle b \rangle$ is an average characteristic growth length (or a unique propagation chain length for this problem) which is independent of time and small compared to the length of the initial amorphous phase. Therefore, it appears correct to reduce the isolation problem of the nitrile groups to a simple combinatorial one.

A probability for m triplets from n cells is

$$P\{n, m\} = \frac{\{(n-3m)+m\}!}{(n-3m)!m!} \times \text{const} \quad (4)$$

where the constant is the normalization factor. For obtaining the most probable m/n , $P\{n, m\}$ must be maximized with respect to m and solve for m/n at that condition. Equation (4) can be solved through the Stirling's approximation.

$$\begin{aligned} \ln P &= \ln(n-2m)! - \ln(n-3m)! - \ln m! + \ln C \\ &= (n-2m)\ln(n-2m) - (n-2m) - (n-3m) \\ &\quad \ln(n-3m) + (n-3m) - m\ln m + m \\ &= (n-2m)\ln(n-2m) - (n-3m)\ln(n-3m) \\ &\quad - m\ln m \end{aligned}$$

Differentiating this equation with respect to m , one gives

$$\begin{aligned} \frac{\partial \ln P}{\partial m} &= -2\ln(n-2m) + \frac{(n-2m)}{(n-2m)}(-2) \\ &\quad + 3\ln(n-3m) - \frac{(n-3m)}{(n-3m)}(-3) - \ln m - \frac{m}{n} \\ &= -2\ln(n-2m) - 2 + 3\ln(n-3m) + 3 - \ln m - 1 \\ &= 3\ln(n-3m) - 2\ln(n-2m) - \ln m = \ln 1 \\ &\quad \text{since } \frac{\partial P}{\partial m} = 0. \quad \text{Hence, } \frac{(n-3m)^3}{(n-2m)^2 m} = 1 \end{aligned}$$

rearranging and dividing this equation by $(1/n)^3$, there is obtained eq. (5).

$$\left(1 - \frac{3m}{n}\right)^3 = \frac{m}{n} \left(1 - \frac{2m}{n}\right)^2 \quad (5)$$

This cubic equation has one real and two conjugate imaginary roots. The value of real root obtained by trial and error is 0.192 (= m/n). This means that 19.2% of the nitrile groups will remain unreacted since I have established on the chemical structural ground that one initiation ring leaves a nitrile group unreactive. Experimentally observed value of 19~22% for the relative concentration of the unreacted nitrile group is in satisfactory accord with this figure.

Furthermore, this finding demonstrates that about 60% of nitrile groups are involved in the initiation and about 20% are destroyed in that step while another 60% are involved in the propagation step.

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