

Isocyanates의 음이온 공중합에 관한 연구

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Studies on the Anionic Copolymerization of Isocyanates

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요 약. DMF 및 NaCN 존재 하에서 *p*-tolylisocyanate와 *n*-hexylisocyanate의 저온 음이온 공중합을 시도하였다. 공중합체의 분자량 및 구조확인에는 각각 삼투압 법과 적외선 법에 의하였다. 공중합체 조성분석도 적외선법에 의하였다. 이 공중합체의 공중합 경향은 M_2 의 반응성이 훨씬 큰 것으로 나타났고 따라서 비 이상형 공중합이었다. 동 mole의 단량체에 의하여 얻어진 공중합체는 rigid한 성질을 나타냈다.

Abstract. The low temperature anionic copolymerization of *p*-tolylisocyanate (M_1) with *n*-hexylisocyanate (M_2) in DMF was carried out with NaCN. Copolymers were characterized by osmometry and I. R. spectrophotometry. Also copolymer composition was analyzed by spectral measurements. The behavior of this copolymerization system was the type of less ideal, that is the M_2 prefers to react exclusively with the same kind of species. The stress-strain behavior of the copolymer obtained from equimolar comonomer feed exhibited somewhat brittle or rigid character.

Introduction

Following an earlier Shashoua's¹ success in synthesizing polyisocyanates by low temperature anionic polymerization of a variety of N-substituted monoisocyanates with NaCN, further various investigations concerning crystallinity or molecular conformations of those homopolymers have been extensively attempted.

It has been considered by several researchers³⁻⁵ that the molecules of *n*-alkyl polyisocyanates possess unusual stiffness and behave as a rigid

rod until when Fetters et al.² have concluded worm-like coil configuration by analyzing molecular weight dependence of the osmotic second virial coefficient and the radii of gyration in terms of the worm-like coil model of Kratky and Porod.

For the aromatic polyisocyanates, Tsvetkov⁶ et al. suggested from the observation of chain stiffness of polytolylisocyanate in bromoform that this aromatic polyisocyanate exhibited random coil configuration.

However, no attempt of conducting copoly-

merization of this series of isocyanates can be found. It is thus the purpose of the present paper to investigate primarily the copolymerization behavior of *n*-hexylisocyanate (*n*HIC) and *p*-tolylisocyanate (*p*TIC).

A preliminary observation of mechanical behavior of the copolymer is also carried out for the purpose of visualizing the possibility of practical use of this series of copolymers.

Experimental

1) Materials: Technical grades of both *p*TIC and *n*HIC from Eastman Organic Chemicals Co. were purified by vacuum distillation after drying overnight over calcium hydride and stored in a refrigerator.

*p*TIC.....95°C at 38 mmHg.

*n*HIC.....67°C at 30 mmHg.

Chemically pure sodium cyanide (Wako Chemicals Co.) was recrystallized three times in water and dried thoroughly.

Dimethyl formamide (DMF) from Kishida Chemicals Co. was vacuum distilled after drying overnight over calcium hydride, 66°C at 38 mmHg.

Methanol from Kishida Chemicals Co. was used after simple distillation.

2) Preparation of Catalyst Solution: The sodium cyanide solution was prepared by dissolving the dry compound in dry DMF to give a saturated solution, 0.68% of NaCN.

3) Polymerization: Table 1 shows representative reaction conditions for homo- and copolymerization. The following is a typical polymerization procedure. To a 100 ml. tubular flask was added the measured amounts of solvent and monomer, and the solution was rigorously degassed with several cycles of melting and freezing. Maintaining evacuation at dry ice temperature, catalyst solution was added by an insertion of hypodermic syringe through a rubber cap fitted at the flask. After brief and vigorous

shaking of flask, polymerization was allowed to proceed at dry ice temperature for periods ranging from 48 to 99 hours with keeping reduced pressure. After termination by releasing evacuation, the polymer was collected by precipitation in methanol. Purification of the polymer was accomplished by several cycles of solubilization in toluene and reprecipitation into methanol. Polymer yields were in the range of 25 to 65 %.

4) Molecular weight determination: Molecular weights of all the products were determined by osmometry. The polymers were dissolved in toluene and osmotic pressures were measured. All measurements were at 37°C. The instrument used was the High Speed Membrane Osmometer, Hewlett Packard Model 501. Vapor Pressure Osmometer, Hewlett Packard Model 302 B, was also used for the determination of molecular weight of cyclic trimer resulted from *p*TIC.

5) Spectral measurement: The infrared spectral measurements were performed with films and KBr pellet method. For the calibration and copolymer composition curve, a definite amount of polymer and KBr were mixed thoroughly and then pelletized to have constant weight. Perkin Elmer, Model 521, was used.

6) Mechanical behavior: Modulus of elasticity, ductility, ultimate strength, and overall stress-strain behavior were evaluated with films (0.02 mm. thickness) by Instron, Model TMS, at room temperature,

Results and Discussion

The representative reaction conditions of various polymerizations, yields, and molecular weights are given in Table 1. Relatively high molecular weight copolymer and homopolymers could be obtained in good yield under anhydrous conditions employing sodium cyanide as the in-

itiator. When reactions were carried out at room temperature, as Shashoua¹ has indicated, no evidence of polymer formation could be detected. Even when the system was strictly controlled to have the same composition and condition except the lowering of reaction temperature, *p*TIC has produced only white crystal of which is approximated in molecular weight with that of cyclic trimer of *p*TIC. In the case of *n*HIC, on the other hand, produced nothing detectable even it was forced to proceed 96 hours duration of reaction at room temperature.

Evidence for the assigned polymer formation

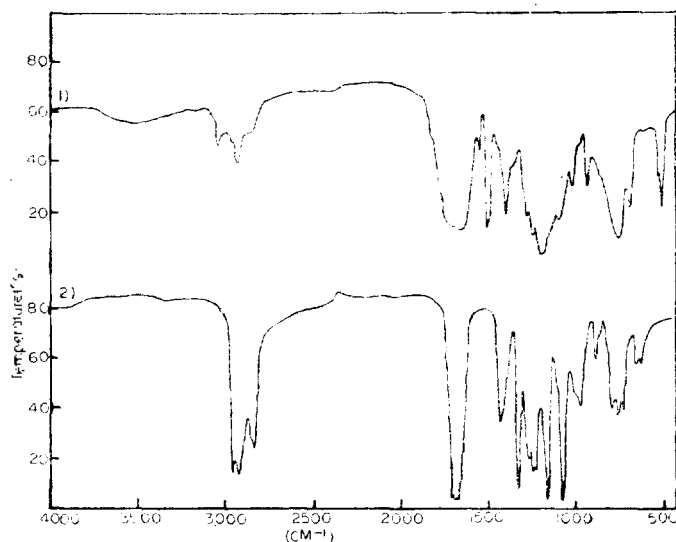


Fig. 1. IR Spectra of homopolymers
1) *p*TIC homopolymer, 2) *n*HIC homopolymer

lies also partly on the interpretation of infrared spectrum. The spectra, in all of the polymer, showed appearances of characteristic and intensive carbonyl absorption bands at near the 1700 cm^{-1} , and conspicuous disappearances of absorption bands at near the 2200 cm^{-1} , corresponding to isocyanate group, as Fig. 1 and 2 depicted. In addition, the fact that the overall shape of *n*-hexyl polyisocyanate in Fig. 1 was quite similar to that of *n*-butyl polyisocyanate obtained by Natta et al⁷, supported indirectly the evidence of polymer formation.

The presence of aromatic composition in copolymer was clearly evidenced by observing the absorptions at 3020 cm^{-1} , due to aromatic C-H stretching, and at 1500 cm^{-1} , due to C to C multiple bond stretching of aromatic ring.

Conversely, with absorptions at $2850\sim 2950\text{ cm}^{-1}$ and at 1450 cm^{-1} , it was able to be interpreted with assurance that those were originated by the effect of aliphatic composition in the copolymer.

Although no accurate analysis of the spectrum obtained from the polymerization of *p*TIC at room temperature is possible, the characteristic complexity of its spectrum especially in the finger print region and the molecular weight calculated lead to a conclusion that this crystal may

Table 1. Reaction conditions of homo-and copolymerization

RNCO	Amount of RNCO (ml.)	DMF (ml.)	Cat. ^a (ml.)	Temp. (°C)	Time (hrs.)	Yield (%)	M _n (×10 ⁻⁴)
<i>n</i> HIC	4	40	1	-70~-75	48.5	63.6	8.60±0.11
<i>p</i> TIC	4	40	1	-72~-76	94	25.0	9.85±0.09
<i>n</i> HIC	2	40	1	-70~-76	99	41.8	7.39±0.16
<i>p</i> TIC	2	40	1	-70~-76	99	41.8	7.39±0.16
<i>n</i> HIC	1	10	0.1	R. temp. ^b	96	Not formed	
<i>p</i> TIC	1	10	0.1	"	96	37.9	0.0336

^a; NaCN in DMF (0.68%), ^b; Room temperature

brought about by cyclization of p TIC.

Since most of the good solvents of homo- and copolymers exhibited absorption bands at near the 1500 cm^{-1} , it was avoided to use solvents for obtaining spectra for the determinations of calibration or copolymer composition curve.

The transmittances at 1500 cm^{-1} of each polymer blends, being composed with such ratios revealed in *Fig. 3*, were measured by applying the base line method and converted them into optical densities by following after the law of Beer-Lambert. These optical densities were then so arranged with the corresponding contents of tolyl polymer as to yield a calibration curve for the determination of copolymer com-

position. As is depicted in *Fig. 4*, a good linear relation was established.

In *Table 2* have been illustrated various conditions and results of copolymerization for composition analysis. Reactions were proceeded to have their conversion rates to be fallen in the range of 3 to 6 % by giving regulation of reaction time. The trend of drastic reduction of tolyl content in copolymer composition even when the amount of tolyl in monomer feed is larger than hexyl has provided evidence of less reactive behavior of tolyl toward the two reacting species.

Fig. 5 shows the intensity variations at 1500 cm^{-1} of initial copolymers. Calculations of these intensities to corresponding absorbances have yielded a curve, having much resemblance⁸ in shape of anionic copolymerization of styrene and M.M. A., of dependence of the instantaneous copolymer composition F_1 on the comonomer feed composition f_1 .

From an observation of the tendency revealed in *Fig. 6*, it was easily conceived that the behavior of this copolymerization might be the type of which one of the monomers is more reactive than the other toward both propagating species.

With equation rearranged in the following form

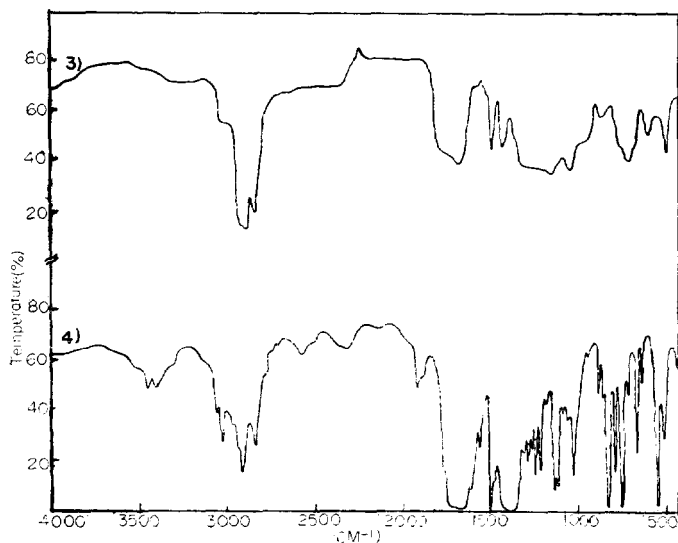


Fig. 2. I. R. spectra of copolymer & trimer
3) Copolymer, 4) Cyclic trimer of p TIC.

Table 2. Copolymerization of p TIC with n HIC in DMF at -76°C . $[\text{NaCN}] = 3.5 \times 10^{-3}\text{ m/l}$

NO	p TIC(m/l)	Monomer n HIC(m/l)	p TIC(mol %)	Time(hrs)	Conversion(wt. %)	Copolymer $\log I_0/I$	p TIC(mol %)
1	0.72	0.08	90	8.5	3.1	0.229	64.0
2	0.67	0.17	80	5.0	4.8	0.193	48.5
3	0.50	0.33	60	3.0	6.2	0.116	15.6
4	0.32	0.48	40	2.5	5.4	0.059	3.6
5	0.17	0.68	20	2.0	4.9	0.044	2.0

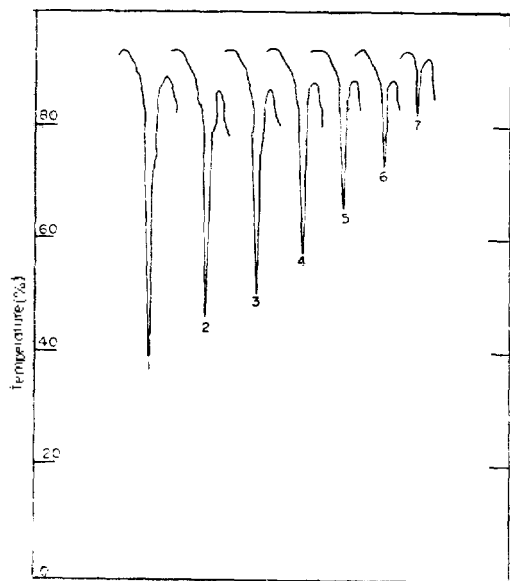


Fig. 3. Intensities of absorption bands of polymer blends at 1500 CM⁻¹.

※ The blend ratios of tolyl to hexyl are as following; 1. 100:0, 2. 80:20, 3. 60:40, 4. 40:60 5. 20:80, 6. 10:90, 7. 5:95.

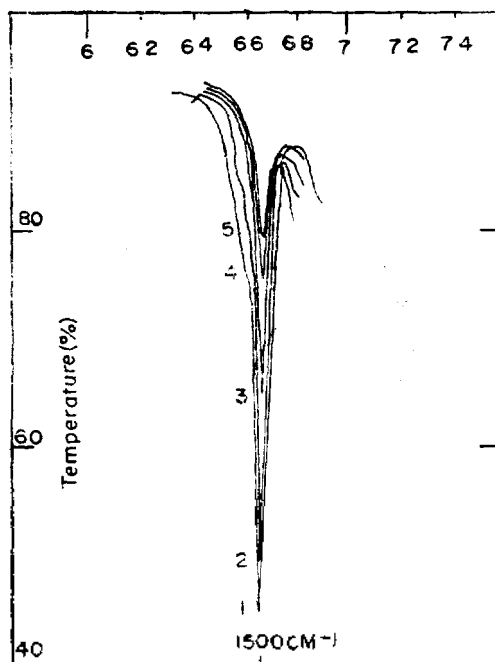


Fig. 5. Intensities of absorption bands of initial copolymers at 1500cm⁻¹. The ratios are monomer feed compositions, tolyl to hexyl.

1. 90:10, 2. 80:20, 3. 60:40, 4. 40:60, 5. 20:80

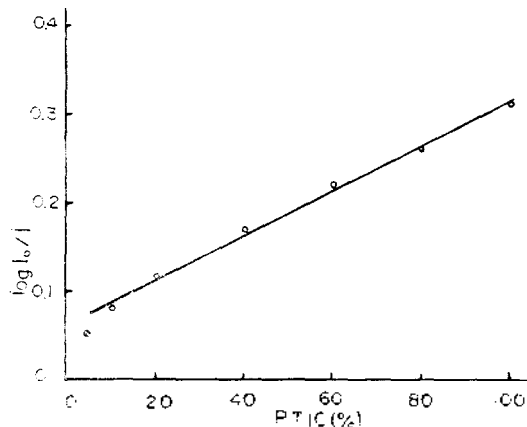


Fig. 4. Calibration curve for copolymer composition determination.

$$\frac{f_1(1-2F_1)}{F_1(1-f_1)} = r_2 + \left[\frac{f_1^2(F_1-1)}{F_1(1-f_1)^2} \right] r_1$$

reactivity ratios for this comonomer pair of *p*TIC (M₁) and *n*HIC (M₂) were calculated. In Fig. 7 have been plotted the values of left side of above equation against the coefficient

or *r*₁, and the least square treatment of such points gives a straight line with slope 0.55(*r*₁) and intercept 16.7(*r*₂).

Although it has been found that the value of *r*₂ derived from Mayo¹⁰ method, as can be seen from Fig. 8, has shown no perfect coincidence with *r*₂ from Fineman⁹, the feature that reactivity ratios shown from both methods is considered to be enough for visualizing the essence of copolymerization behavior of this comonomer pair. The propensity associated with above reactivity ratios leads to a conclusion that the selectivity of *n*HIC toward the two reacting species in DMF is obviously greater than the *p*TIC, that is the behavior of anionic copolymerization of this comonomer pair is rather the type of less ideal.

From the structural point of view, it was expected that the reactivity order of *p*TIC would be higher than *n*HIC owing to the resonanc stabilization of tolyl anion. The reason, however, that the behavior of this copolymerization system turned out to be the reverse of above prediction was postulated as the reactivity of this system might be influenced by the reaction condition, as is often encountered in ionic copolymerizations.

Mechanical behaviors of copolymer containing about 10 % of tolyl content in copolymer are illustrated in Fig. 9. Films of 0.02 mm. thick-

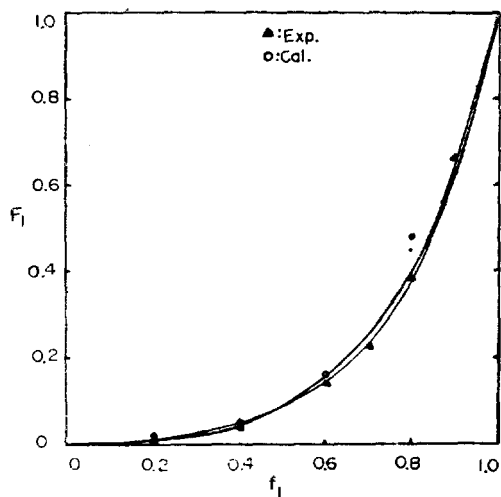


Fig. 6. copolymer composition Curve.
O; Exp., \blacktriangle ; Cal.

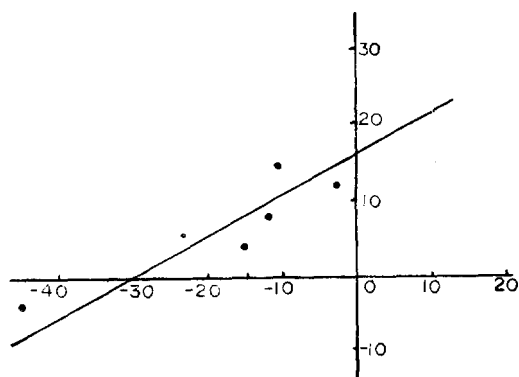


Fig. 7. Reactivity ratios (from Fineman et al.)
 $y=16.7+0.55x$

ness were casted from a toluene solution and used for the measurements.

As is apparent from the Fig. 9, the stress-strain behavior in tension can be viewed as a demonstration of somewhat brittle and rigid character. This rigid behavior is considered to be originated by the influence of predominant alkyl segment which is known to have worm-

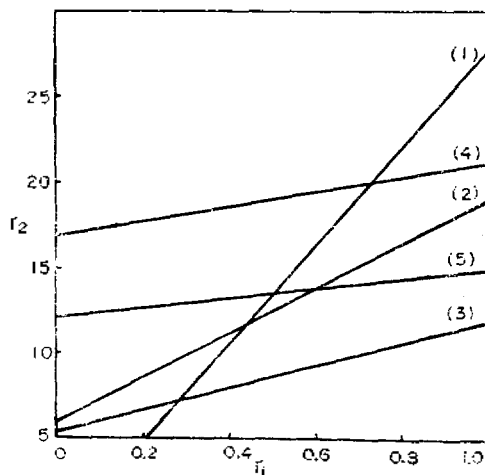


Fig. 8. Reactivity ratios (from Mayo et al.)

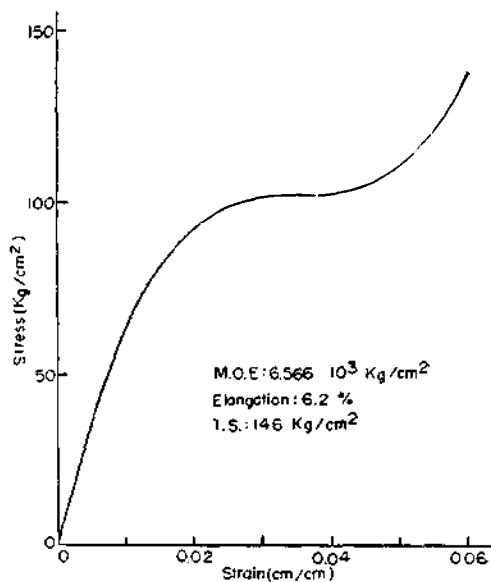


Fig. 9. Stress-strain curve of copolymer
M. O. E: Modulus of elasticity
T. S.: Tensile strength

like coil or rod-like configuration. It is thus presumed that the modification of copolymer segment as to have more domain of tolyl segment whose configuration is known as a random coil may contribute to form material producing desirable properties for practical purpose like fiber.

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Reference

1. V. E. Shashoua, W. Sweeny, and R. T. Tietz, *J. Amer. Chem. Soc.*, **82**, 866 (1960).
2. L. J. Fetters, and Hyuk Yu, *Macromolecules*, **4**, 385 (1971).
3. N. S. Schneider, and S. Furusaki, *J. Poly. Sci.*, **3A** 933 (1965)
4. V. W. Burchard, *Makromol. Chem.*, **67**, 182 (1963).
- 5) H. Yu, A. J. Bur, and L. J. Fetters, *J. Chem. Phys.*, **44**, 2568 (1966).
- 6) C. N. Tsvetkov, *Eur. Polym. J., Suppl.*, 237 (1969).
- 7) G. Natta, J. Dipietro, and M. Cambini, *Makromol. Chem.*, **56**, 200 (1962).
8. G. Odian, "Principles of polymerization" P. 371 McGraw-hill book Co., New York, 1970.
9. *ibid.*, P. 383.
10. F. R. Mayo, and F.M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).