ADVANCES IN URETHANE SCIENCE AND TECHNOLOGY

VOLUME 8

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K.C. Frisch
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Polymer Institute
University of Detroit

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DR. SIDNEY L. REEGEN

In Memoriam

The scientific community and in particular the Polymer Institute of the University of Detroit suffered a great loss with the death of Dr. Sidney L. Reegen in November, 1979. Dr. Reegen was co-editor of seven volumes of the series, "Advances in Urethane Science and Technology."

Dr. Reegen's distinguished career spanned 15 years in industry and 11 years in academia. A graduate with a B.S. in Chemistry from the City University of New York in 1946, he obtained an M.S. in Organic Chemistry from the Polytechnic Institute of Brooklyn (now Polytechnic University of New York) in 1949 and a Ph.D. in Polymer Chemistry from the same institution in 1952 with Professor F.R. Eirich as thesis advisor.

He started his industrial career with the Industrial Rayon Corporation in Cleveland (1953-1958) and joined the General Motors Research Laboratories in Warren, Michigan, in 1958. He spent there four years as Supervisor in the Polymer Research Department. He joined Wyandotte Chemicals Corporation (now BASF-Wyandotte) in 1962 where he became a Project Leader in the Polymer Research and Development Department.

While working in industry, Dr. Reegen taught courses at the Detroit Institute of Technology (1961-1962) and at Lawrence Institute of Technology (1965-1968).

Dr. Reegen became a staff member of the Polymer Institute of the University of Detroit in August, 1968, where he became a Research Professor and served also as Associate Director of the Polymer Institute and as Director of the Polymer Conferences at the University of Detroit. He was also instrumental in the organization of Minority Courses for Plastics Technicians at the Polymer Institute.

Professor Reegen's outstanding research activities were in many diversified polymer areas, notably polyurethanes, polyamides and polyesters. Special areas of research also included basic studies in polyurethane adhesives, films, coatings, foams and water-soluble polymers. He also carried out a series of excellent investigations on the formation of complexes between urethane catalysts and isocyanates and alcohols. The results of his investigation were published in many scientific journals and books. He co-edited a book on "Ring Opening Polymerization" and had a number of U.S. and foreign patents to his credit.

Dr. Reegen was very active in professional societies, among them the American Chemical Society, Society of Plastics Engineers, Federation of Societies for Coatings Technology, Great Lakes Conferences on Polymers and Colloids, Society of Automotive Engineers and others.

Dr. Reegen was also very active in civic affairs and was highly esteemed by both his friends and professional colleagues who cherished his human qualities.

CONTENTS

ISOCYANURATE FOAM:
THE ROLE OF THE ISOCYANATE AND CATALYST

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CAVEAT

This paper deals in part with flammability test performance. These references should be used solely as a measure and description of the properties of materials, products or systems in response to heat and flame under controlled laboratory conditions. They should not be considered or used for the description, appraisal or regulation of the fire hazard of materials, products or systems under actual fire conditions.

INTRODUCTION

Since its commercialization in the early 1960's, rigid urethane foam has achieved wide acceptance as an efficient thermal insulation. During this period, numerous technical advancements have been made in the formulation and processing of these foam plastics. These improvements have broadened the serviceability of rigid urethane foams and have overcome most of the major deterrents to even wider acceptance in the thermal insulation market.

Among the more recent achievements in the urethane industry is the development of improved flame retardant foams to meet the current flammability standards. One approach to flammability improvement has been to increase the thermal stability of the polymer through the use of the isocyanurate chemical linkage.

Isocyanurate foams are generally recognized as being superior to rigid urethane foams in terms of flammability, thermal stability, and dimensional stability. Unfortunately, most commercially available isocyanurate systems have also displayed various undesirable characteristics which overshadow these advantages. High friability, poor adhesion and narrow processing latitude have hindered the broad utility of isocyanurate foams in most applications.

The production of a faced insulation panel by the continuous lamination process is one such application. This method of production is popular because of its efficiency and versatility. In addition, through the proper selection of facing materials, the resulting boardstock can be tailored to meet specific performance requirements; e.g. structural strength, indentation resistance, reflectivity, vapor barrier performance, etc.

1

Through the proper selection of the isocyanate and the catalyst the utility of isocyanurate foams can be significantly increased in this type of application.

BACKGROUND

Isocyanurate is an excellent structural unit for cellular plastics because of its high decomposition temperature. Pure isocyanurate foam has good thermal stability and low flammability, but is too friable and difficult to process to be of commercial value and thus requires the introduction of other chemical groups such as urethane to modify its properties. The objective of introducing urethane groups is to improve friability and processability while preserving thermal stability and low flammability. All commercially available isocyanurate foams are urethane modified.

The concentration of isocyanurate rings in an isocyanurate/urethane foam can be conveniently expressed as the percent by weight of free NCO, in the polymer mixture that is available for conversion to isocyanurate. That is,

$$\% \text{ Isocyanurate} = \frac{\left(\dfrac{\text{wt. of A}}{\text{Eq. wt. of A}} - \dfrac{\text{wt. of B}}{\text{Eq. wt. of B}} \right) \times 42 \times 100}{\text{wt. of A} + \text{wt. of B}}$$

where A is the isocyanate and B is the polyol. In the case of an unmodified or pure isocyanurate foam, the % isocyanurate is simply the free-NCO content of the isocyanate.

$$\% \text{ Isocyanurate} = \frac{42}{\text{Eq. wt. of A}} \times 100 = \% \text{ free NCO}$$

Unmodified isocyanurate foams made from several commercially available isocyanates were tested for friability in accordance with ASTM D-421 and flammability in terms of burn extent in the Monsanto tunnel [1]. In this test, conventional non-flame retardant urethane foam burns in excess of 23 inches (length of the tunnel), while moderately flame retardant conventional foams burn 15-20 inches. The data presented in Table 1 indicates that unmodified isocyanurate foams display excellent flammability, but very high friability.

Mondur MR isocyanate was selected to study the effect of reduced isocyanurate levels on flammability and friability. The introduction of urethane linkages was accomplished by adding increasing levels of ethylene glycol. The results of this study are shown in Table 2. Reducing the isocyanurate content decreases friability and increases flammability. The minimum level

2

Table 1. Unmodified Isocyanurate Foams.

Isocyanate	% Isocyanurate	Density lbs/ft³	Monsanto Tunnel Burn Extent Inches **	Friability % Wt. Loss
Isonate 135	30.2	1.91	8.2	89
Mondur MR	30.5	1.90	8.4	82
Hexacal F	28.8	1.91	8.1	89
Isonate 143L	29.0	1.84	8.8	73
ACB***			5.5	
Control*			9.6	42

*Control is a commercial isocyanurate bun stock foam having an ASTM E-84 flame spread of 25.

**These numerical flame spread ratings are not intended to reflect fire hazards presented by this or any other material under actual fire conditions.

***Asbestos Cement Board.

Table 2. Urethane Modified Isocyanurate Foams (Conventional Isocyanate and Ethylene Glycol).

% Isocyanurate	Monsanto Tunnel Burn Extent Inches**	Friability % Wt. Loss
30.5	8.2	89
24	8.4	46
22	8.8	40
20	10.1	30
18	10.6	23
16	-	17
14	12.2	11
Control*	9.6	42

*Control is a commercial isocyanurate bun stock foam having an ASTM E-84 flame spread of 25.

**These numerical flame spread ratings are not intended to reflect fire hazards presented by this or any other material under actual fire conditions.

Table 3. Effect of Various Glycols on Friability and Flammability of 22% Iso-
cyanurate Foam Using Mondur MR.

Glycol	Friability % Wt. Loss	Monsanto Tunnel Burn Extent Inches**
Ethylene	35	10.0
Diethylene	25	10.0
Triethylene	5	10.4
Tetraethylene	12	10.9

**These numerical flame spread ratings are not intended
to reflect fire hazards presented by this or any other
material under actual fire conditions.

of isocyanurate which has a burn extent in the Monsanto tunnel comparable
to that of a 25 flame spread rated control is approximately 20-22%. At this
level, using ethylene glycol, friability is too high (30-40%) for commercial use.
The effect of several other simple glycols on friability and flammability is
presented in Table 3. The data shows that at a constant isocyanurate level of
22%, friability decreases and flammability increases as equivalent weight in-
creases. The effect on flammability is slight which supports the proposition
that flammability is primarily a function of isocyanurate level. Of the simple
glycols, the data suggests that diethylene glycol furnishes the best com-
promise between friability and flammability.

Table 4 summarizes the test results of foams made at approximately 20%
isocyanurate using various polyols. Mondur MR was the isocyanate used for
these experiments. It appears that the nature of the polyol has no significant
effect on flammability, but it does affect friability. However, the friability level
was still unacceptable (20%-30%) for commercial applications.

In order to produce a commercially suitable isocyanurate foam, the com-
mon practice has been to reduce the isocyanurate level [2,3] and sacrifice in-
herent fire retardant characteristics to achieve low friability. Low flammability
is then regained through the addition of fire retardant additives. This ap-
proach, however, has two major drawbacks. First, fire retardant additives
generally increase smoke evolution and second, both the reduced

Table 4. Effects of Polyol Structure.

Polyol (Eq. Wt.)			% Isocyanurate	Monsanto Tunnel Burn Extent Inches**	Friability % Wt. Loss
Et	$(OH)_2$	(31)	19.5	10.6	27
1,2-Pr	$(OH)_2$	(38)	19.5	11.1	29
1,3-Pr	$(OH)_2$	(38)	19.5	11.0	22
1,4-Bu	$(OH)_2$	(45)	19.5	10.9	26
2,3-Bu	$(OH)_2$	(45)	19.5	10.7	39
1,2,6-Hex	$(OH)_3$	(45)	19.5	10.7	76
$\dfrac{1,2\text{-Pr} \quad (OH)_2 \ (50)}{G\text{-}2406^*}$			19.5	10.8	29
TE-270*		(89)	17.1	11.3	12
PeP-650*		(153)	19.7	--	42.6
RS-350*		(157)	20.5	11.4	69.4

*Commercially available polyether polyols:
G-2406-sorbitol polyol @87 eq. wt.,
TE-270-ethoxylated triol @89 eq. wt.,
PeP-650-pentaerythritol polyol @153 eq. wt.,
RS-350-sucrose polyol @157 eq. wt.

**These numerical flame spread ratings are not intended to reflect fire hazards presented by this or any other material under actual fire conditions.

isocyanurate level and the presence of fire retardant additives have a detrimental effect on the thermal stability of the polymer and the dimensional stability of the foam.

The alternate approach, which is the subject of this paper, is to maintain a high isocyanurate level and to reduce friability through modification of the polymeric isocyanate without affecting flammability, thermal stability or smoke evolution. The modifications that were studied were directed at overcoming the major disadvantages of high isocyanurate content foams made from commercially available polymeric isocyanates. These were:

1. Processing difficulties on equipment commercially used for foamboard manufacture.

2. Coarse celled, striated foams having low strength and high friability.

The processing difficulties were attributed primarily to low chemical system viscosity. Typical urethane system viscosity is 250-500 cps while high

isocyanurate content systems are in the range of 75-150 cps. Low system viscosity is not conducive to depositing a uniform layer of chemicals between the facers, which is an important step in continuous lamination processes. Low viscosity also tends to promote drainage from the cell windows, resulting in coalescence and coarse, striated cell structure. Increased chemical system viscosity was, therefore, expected to be beneficial not only to processability but also to several other foam properties.

The manufacture of boardstock foam insulation by the continuous lamination process also requires that the chemical mixture stay liquid long enough to go through metering rolls. Subsequent expansion and hardening of the foam must occur prior to reaching the cut-off saws. In most laminating lines this distance is fixed. Therefore, the time elapsed between metering the chemicals at the nip rolls and cutting of the board only varies with line speed. The requirement of a long cream time followed by fast firm time are very demanding, and catalyst combinations are commonly used since single catalysts do not drive both reactions at a rate suited for this type of process. Finding a catalyst system that yields a good balance between processability, conversion, and foam properties is very important.

The catalyst work reported in the literature for utilizing the isocyanurate linkage in the production of foam insulation boardstock is limited. In most of this catalyst work, tertiary amines, metal carboxylates, alkoxides and diepoxides were reported to be the most efficient; however, most of the work was done in solution and not under actual foaming conditions.

Nicholas and Gmitter reported in 1965 [4] the synthesis of various urethane-modified isocyanurate foams using TDI prepolymers with various tertiary amine and tertiary amine/diepoxide combinations as catalysts. In 1968 G.W. Ball [5] and coworkers reported on various isocyanurate foams but without reference to the formulation. The catalyst was described as a basic substance. Beitchman [6] reported in 1966 the effect of various tertiary amines on the rate of isocyanurate formation in solution. Reymore [3] et al in 1975 reported on a variety of catalysts for the trimerization of isocyanates but there were no details concerning the efficiency or effect of these catalysts on the reaction profile. More recently, Bechara and coworkers [7] reported on the use of hydroxyalkyl quaternary ammonium carboxylates to trimerize phenyl isocyanate in solution.

The development of various catalyst systems for the production of urethane-modified isocyanurate foam insulation boardstock by the continuous lamination process is another subject of the paper.

RESULTS & DISCUSSION

Part I — The Role of the Isocyanate

Prepolymer — The first method selected to evaluate the effect of

6

Table 5. *Effects of Increased Chemical System Viscosity.*

	Low Viscosity Isocyanate	Prepolymer	High Viscosity Isocyanate
System Viscosity, cps	100	300	300
% Isocyanurate	22	22	22
Density, lb/ft^3	1.8	1.8	1.7
Friability, % Wt. Loss	23	10	10
ASTM E-84 Tunnel**			
F.S.V.	20	18	18
Smoke	60	54	25
Dimensional Stability Maximum Linear Growth, %			
70°C/95% RH	3.2	5.3	3.8
125°C	4.2	5.7	6.2
TGA, Wt. Loss %*	18	18	18

*Wt. Loss in % between 250°C-300°C.

**These numerical flame spread ratings are not intended to reflect fire hazard presented by this or any other material under actual fire conditions.

increased chemical system viscosity involved the use of an isocyanate prepolymer. A small amount of ethylene glycol was pre-reacted with Mondur MRS. The resulting prepolymer had a viscosity of 2000 cps @ 25°C. Table 5 shows a comparison between foams made with this higher viscosity prepolymer system and an equivalent one-shot system based on diethylene glycol and Mondur MRS. There was a very significant improvement in processability with the prepolymer system; in addition, the foam had a fine, uniform cell structure and a significant reduction in friability was observed with no adverse effect on flammability or thermal stability.

    Higher Viscosity Isocyanate — Based on the results of the prepolymer study, various high viscosity isocyanates were obtained from several suppliers. One-shot systems based on these materials yielded results similar to the systems using prepolymers. Table 5 shows physical properties of a foam made with one of these high viscosity polymeric isocyanates.

Table 6. Effect of Isocyanate on Foam Properties.

Sample No. ***	3	1	2	4
% Isocyanurate	22	22	22	22
Density, lb/ft.^{3}	1.82	1.80	1.80	1.80
Friability, % wt. loss	27	21	15	20
Oxygen Index*	27.3	26.3	25.8	26.5
ASTM E-84 Tunnel**				
F.S.V.	---	21	28	---
Smoke	---	49	63	---
Distortion Temperature, °C	160	155	123	---

*Measured according to ASTM D-2863-70 except that a sample measuring 1/2 inch x 1/2 inch x 6 inches is used. The values obtained are not intended to reflect fire hazard under actual fire conditions.

**These numerical flame spread ratings are not intended to reflect fire hazard presented by this or any other material under actual fire conditions.

*** For analytical properties see Table 8.

The effect of varying the isocyanurate level in a system based on one of these high viscosity isocyanates and diethylene glycol was similar to the previous experiment using Mondur MR and ethylene glycol. This data is presented in Table 7. The data again suggests that an isocyanurate level of 20-22% yields optimum flammability. The friability results, however, are considerably improved over those presented in Table 2 and represent the combined effects of the isocyanate modification and the change to diethylene glycol.

All high viscosity isocyanates improved processability. However, foams generated from the various isocyanates differed in physical properties. Comparative physical property data is presented in Table 6. Variations were particularly evident in friability, flammability, and thermal stability. Thermal stability was determined through the use of a Gaertner Quartz-tube Dilatometer. The Gaertner Quartz-tube Dilatometer consists of two tubes constructed of fused quartz, one fitting within the other, and a dial gauge

Table 7. *Urethane Modified Isocyanurate Foam (High Viscosity Isocyanate and Diethylene Glycol).*

% Isocyanurate	Monsanto Tunnel Burn Extent Inches**	Friability % Wt. Loss
14.5	13.1	7
15.8	12.2	-
17.1	10.6	-
18.4	9.3	11
19.4	8.5	-
20.4	8.5	11
21.3	8.3	16
Control*	9.6	42

*Control is a commercial Isocyanurate Bun Stock Foam having an ASTM E-84 flame spread of 25.

**These numerical flame spread ratings are not intended to reflect fire hazards presented by this or any other material under actual fire conditions.

mounted so as to measure the relative displacement as one tube moves within the other. A cylindrical specimen, measuring ½" in diameter × 2" in length, is placed in the bottom of the outer tube and the inner tube is inserted with its lower end contacting the specimen. The gauge is adjusted until its stem touches the upper end of the inner tube. The dilatometer is then placed in a furnace where the temperature is increased at a rate of 4-10°C per minute. As the specimen expands or contracts, the movement of the inner tube is registered by the gauge. Foams based on several polymeric isocyanates in equivalent formulations were evaluated using this procedure. A plot of temperature vs change in height is shown in Figure 1. The inflection point of these curves represents the distortion temperature.

Infrared analysis of these foams indicated that they all contained some level of unreacted isocyanate. Obviously, not all the available isocyanate was being converted to isocyanurate. An analytical procedure normally used to measure the amine equivalent of a polymeric isocyanate was modified to measure the amount of unreacted isocyanate in a freshly manufactured foam specimen, thus quantifying the conversion level. This was done by allowing a finely ground foam specimen to react with excess n-butylamine and back-titrating with dilute HCl. In calculating the % conversion it is assumed that the
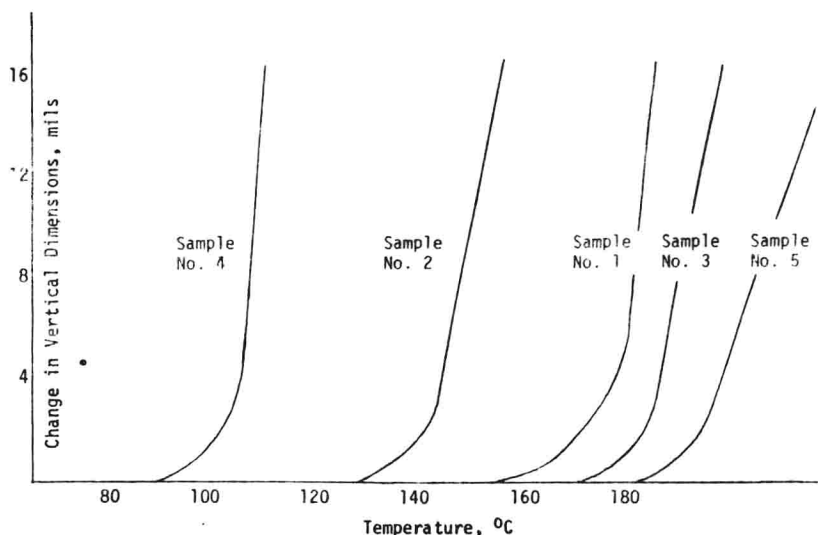
Figure 1. Dilatometer Experiments.

urethane reaction goes to completion and that the measured quantity of unreacted isocyanate represents an incomplete trimerization reaction. The calculation for % Conversion then becomes:

$$\% \ \text{Conversion} \ = \ \frac{\text{Theoretical} \quad \% \ \text{by weight free NCO}}{\text{Theoretical} \ \% \ \text{Isocyanurate}} \ \times \ 100$$

It was proposed that the observed differences in physical properties were caused by differences in the level of conversion achieved with the various iso-cyanates being studied. In addition, it was suspected that the conversion level associated with a particular polymeric isocyanate was dependent upon a specific property or set of properties which characterized the isocyanate.

In addition to % conversion, each of the polymeric isocyanates was analyzed for all properties which were known or suspected of having some effect on conversion. A general analysis of this data which is presented in Table 8 leads to the following conclusions:

Acidity — Acidity does not affect conversion (except perhaps in extreme cases). However, it does increase catalyst consumption. Low acidity is desirable to minimize catalyst usage. Acidity should be less than 0.08% HCl.

Table 8. Characterization of Polymeric Isocyanates.

Sample No.	1	2	3	4	5	6
Amine Equivalent	137.4	143.5	136	140.9	134	134
Acidity as % HCl	.02	.08	.03	.08	.03	.06
Viscosity, cps @25°C	2000	2000	850	800	250	250
% Carbodiimide	2.2	3.8	1.5	2.1	ND*	ND*
Molecular Wt. Distribution						
By LC.						
% MDI	27.3	28.0	32.1	34.1	40.6	45
MDI Isomer Distribution						
By Gas Chromatography						
% p,p'	97	100	96	98	97	77
Foam Reactivity (Hand Batch)						
Catalyst Wt., g	11	11	10	15	12	12
Cream, sec.	18	17	18	20	20	19
Firm, sec.	33	34	36	37	34	33
Tack-free, sec.	50	45	65	--	39	38
Max. Exotherm, °C	140	142	160	175	195	184
Distortion Temperature, °C	157	126	164	94	172	ND*
% Conversion	72	51	81	71	89	68

*ND = Not Determined

Amine Equivalent — This is not an independent variable. However, the trend is that low eq. wt. yields higher conversion. It is interesting to note that the limiting equivalent wt. of a methylene bridged polyphenyl polyisocyanate is 131. All commercially available polymeric isocyanates have equivalent weights higher than 131. Thus, other groups must be present to increase equivalent weight. The presence of carbodiimide and dimer, both of which will increase equivalent weight, are evidenced by the characteristic IR bands of these two linkages at 2120 cm⁻¹ and 1790 cm⁻¹, respectively.

Viscosity — A high viscosity isocyanate is essential to eliminate the processing problems of a high isocyanurate content chemical system. The data in Table 7 indicates that as viscosity increases, conversion decreases. Thus, improved processability is achieved at some sacrifice to conversion. However, viscosity is not an independent variable but rather it depends on other characteristics of the isocyanate such as molecular weight distribution and carbodiimide content.

Molecular Wt. Distribution — This is the wt. % of each molecular fraction that makes up the polymeric isocyanate as determined by a new liquid-liquid chromatography technique [8]. Specifically, it refers to the proportion of MDI, triisocyanate and other methylene bridged polyphenyl polyisocyanates present. The results are intended to be used for comparative purposes and may not reflect absolute composition.

Ideally, both high viscosity and high MDI content are desirable. However, the data clearly indicates that increased viscosity is gained at some sacrifice

Table 9. Effect of % MDI on Conversion.

Molecular Wt.
Distribution

% MDI	40.6	35.4	31.6	28.8	27.3
% 3 Ring	33.3	33.8	33.4	32.3	35.7
% 4 Ring	25.4	24.5	24.7	24.6	24.6
% 5 Ring	1.12	11.3	10.4	14.4	12.6
% 6 Ring	Trace	Trace	Trace	Trace	Trace
Viscosity cps @ 25°C	250	700	1000	1500	2000
Max. Exotherm, °C	154	144	142	134	133
% Conversion	90	85.6	81.2	79.6	71.8
Foam Density, lb/ft^3	1.75	1.80	1.83	1.90	1.83
% Closed Cells	88	88	89	88	89

to MDI content. As % MDI decreases, molecular conversion decreases, as shown in Table 9. In addition, the data (see Table 8) suggests that increased viscosity is characterized by increased levels of higher molecular weight fractions. These compounds are presumed to be primarily methylene bridged polyphenyl polyisocyanates. There is, however, evidence of such other components as carbodiimide. The presence of this latter moiety appears to have a negative effect on conversion. This is evidenced by comparing the conversion level and analytical properties of samples 1 and 2. Both have approximately the same viscosity and MDI content, but sample 1 has a lower carbodiimide content and exhibits a higher conversion. Similarly, the difference in conversion between sample 4 and isocyanate sample 3 can be attributed to the difference in carbodiimide content.

MDI Isomer Distribution — Although sample 6 has the highest MDI content of the isocyanates evaluated, it does not show the highest conversion. This can be explained through MDI isomer distribution. Sample 6 shows a much lower p,p′ level in the MDI component and a higher level of ortho-position NCO in the MDI fraction than the other isocyanates. This suggests that the higher molecular weight fractions of sample 6 are terminated by the same proportion of ortho-positioned NCO groups. An ortho-positioned NCO should be less capable of trimerizing than the para-positioned NCO because of steric hindrance.