

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

¹³C-NMR Sequence Analysis. XIV. Ternary Aliphatic Copolyamides

Hans R. Kricheldorf^a; William E. Hull^b

^a Institut für makromolekulare Chemie der Universität, Freiburg, Germany ^b Bruker-Physik AG, Rheinstetten, Germany

To cite this Article Kricheldorf, Hans R. and Hull, William E. (1977) '¹³C-NMR Sequence Analysis. XIV. Ternary Aliphatic Copolyamides', *Journal of Macromolecular Science, Part A*, 11: 12, 2281 – 2292

To link to this Article: DOI: 10.1080/00222337708061364

URL: <http://dx.doi.org/10.1080/00222337708061364>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

¹³C-NMR Sequence Analysis. XIV. Ternary Aliphatic Copolyamides

HANS R. KRICHELDORF

Institut für makromolekulare Chemie der Universität
D-7800 Freiburg, Germany

and

WILLIAM E. HULL

Bruker-Physik AG
D-7512 Rheinstetten, Germany

ABSTRACT

Ternary copolyamides were obtained either by anionic copolymerization of ϵ -caprolactam, ω -capryllactam, and ω -laurinlactam or by cocondensation of AH-salt with ϵ -caprolactam and ω -laurinlactam. These copolyamides contain nine different amide groups which can be identified by their CO-signals in the 90.5 MHz ¹³C-NMR spectra. From the intensities of the CO signals, the ratio of monomer units in the copolymers and hence the reactivity of the monomers can be estimated. Furthermore, the average length of the homogeneous blocks can be calculated.

INTRODUCTION

In previous papers of this series we have demonstrated that alternating sequences of various ω -amino acids can be characterized by their ^{13}C -NMR spectra [1-4]. This characterization is based on the CO signals which show different shifts for alternating copolyamides and mixtures of the corresponding homopolyamides. Binary random copolyamides were analyzed in a similar manner, since they contain likewise homogeneous (A-A, B-B) as well as heterogeneous amide bonds (A-B, B-A) which can be distinguished by their CO signals [5, 6].

Copolymerization of three suitable monomers should lead to ternary copolyamides which contain nine different amide groups, if each monomer has reacted with itself and with both other monomers. It is the purpose of this paper to examine to what extent ternary copolyamides can be analyzed by ^{13}C -NMR spectroscopy. Two different kinds of copolyamides were studied, namely, a product resulting from anionic copolymerization of three lactams and a product resulting from cocondensation of AH-salt and two lactams.

EXPERIMENTAL

Polymer Synthesis

Nylon 6/8/12. A mixture of 50 mmole portions of ϵ -caprolactam, ω -capryllactam, and ω -laurinlactam was melted at 150°C . Then 200 mg sodium was dissolved in this melt and 0.2 ml benzoyl chloride was added. This mixture was kept at 150°C for 1 hr and thereafter at 200°C for 10 hr. The resulting copolyamide was dissolved in 150 ml formic acid, precipitated from 1.5 liter tetrahydrofuran and dried at $80^\circ\text{C}/10^{-2}$ mbar; yield: 35%.

Nylon 6/66/12. A mixture of 50 mmole portions of ϵ -caprolactam, of AH-salt, and of ω -laurinlactam was first heated for 0.5 hr at 200°C under a slow stream of nitrogen and then for 8 hr at 260°C . The reaction product was dissolved in 150 ml formic acid, precipitated from 1.5 liter tetrahydrofuran, and dried at $80^\circ\text{C}/10^{-2}$ mbar; yield: 30%. A similar experiment was carried out with a mixture of 100 mmole ϵ -caprolactam, 50 mmole AH-salt, and 50 mmole ω -laurinlactam; yield: 50%.

Measurements

The ^{13}C -NMR spectra of all copolyamides were measured on a Bruker WH-360 FT-NMR spectrometer at a magnetic field strength

of 84 kGauss. A pulse width of 20 μ sec ($\sim 80^\circ$) was used, and ca. 3000 scans were accumulated with 32 K data points for a spectral width of 18000 Hz if the total spectrum was measured or about 2000 scans with 2 K data points for 600 Hz, if only the carbonyl region was measured. Solutions of 500 mg polyamide in 2.5 ml fluorosulfonic acid were measured in 10 mm diameter sample tubes equipped with a 4 mm coaxial capillary containing a 1:1 mixture of dioxane- d_8 and TMS.

RESULTS AND DISCUSSION

Qualitative Evaluation of the NMR Spectra

The anionic copolymerization of ϵ -caprolactam (azepinone-2), ω -capryllactam (azanonanone-2), and ω -laurinlactam (azatridecanone-2) at 200°C was not quantitative after 10 hr. This result was desired, since under this condition the resulting nylon 6/8/12 terpolymer should contain the monomer units in different ratios, depending on their reactivity. The same is true for the ternary copolyamides resulting from the cocondensation of ϵ -caprolactam, AH-salt, and ω -laurinlactam (1:1:1 and 2:1:1) at 250°C. As expected, the solubility of these ternary copolyamides is much better than that of the corresponding homopolyamides, so that they can be dissolved in common NMR solvents like trifluoroacetic acid, formic acid, methanol, and hot dimethyl sulfoxide. However, their ¹³C-NMR spectra were measured in fluorosulfonic acid, since a previous investigation on binary copolyamides proved that this solvent and concentrated sulfuric acid give the best resolution of the CO signals.

Since under the reaction conditions chosen all monomers should be able to react with themselves and with each other, the resulting ternary copolyamides should contain nine different kinds of amide groups. Hence, a maximum of nine CO signals is expected in their ¹³C-NMR spectra. As shown in Fig. 1, the 90.5 MHz ¹³C-NMR spectrum of nylon 6/8/12 exhibits seven clearly resolved CO signals plus two shoulders, while in the case of nylon 6/66/12 (Fig. 2) all nine CO signals are resolved. The assignment of all CO signals was achieved by comparison of their chemical shifts with the shifts of corresponding binary copolyamides and homopolyamides (equal the homogeneous blocks in the copolyamides). The 90.5 MHz ¹³C-NMR spectra of homo- and binary copolyamides exclusively prepared from lactams are described in a previous paper [6]. The 90.5 MHz ¹³C-NMR spectra of nylon 66/12 and nylon 6.6/6 in fluorosulfonic acid were measured now for a comparison with nylon 6/6.6/12, since previously only 22.6 MHz spectra of these copolyamides in concentrated sulfuric acid were reported [5]. It was found that the shifts

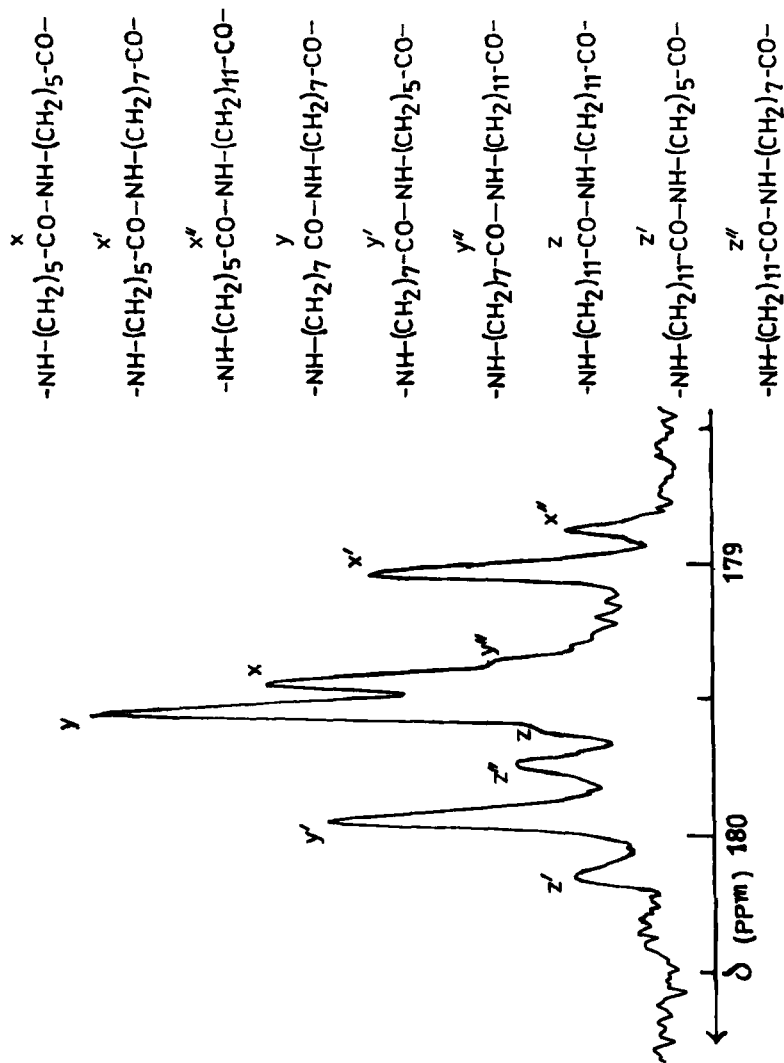


FIG. 1. CO signals in the ^{13}C -NMR spectrum (90.5 MHz, FSO_3H) of nylon 6/8/12 prepared from a 1:1:1 mixture of ϵ -caprolactam, ω -capryllactam, and ω -laurinlactam.

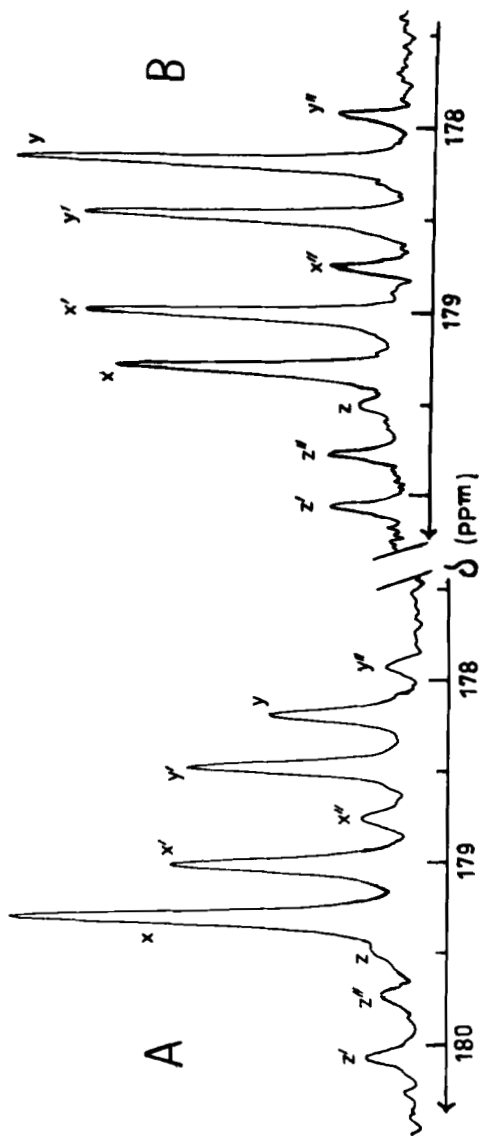
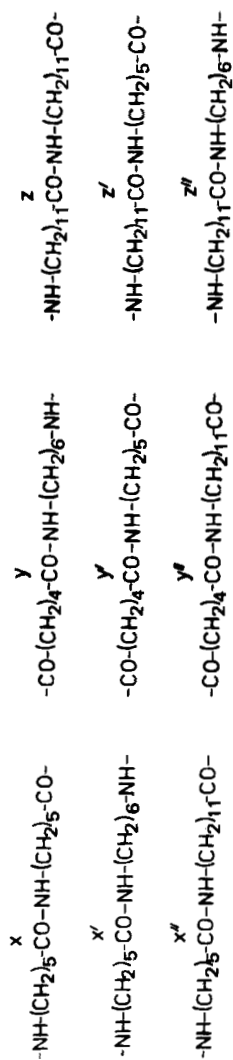


FIG. 2. CO signals in the ¹³C-NMR spectra (90.5 MHz, FSO₃H) of nylon 6/66/12 prepared from (A) a 2:1:1 mixture of ε-caprolactam, AH-salt and ω-laurinlactam; (B) a 1:1:1 mixture of the same monomers.

TABLE 1. ^{13}C -NMR Chemical Shifts δ of CO Signals from Homopolymers and Random Copolyamides in Fluorosulfonic Acid at 30–35°C

Polymer	δ (ppm, relative to external TMS)										
	Nylon 6 residue			Nylon 8 or nylon 66 residue			Nylon 12 residue				
	x	x'	x''	y	y'	y''	z	z'	z''		
Nylon 6	179.26										
Nylon 8				179.42							
Nylon 12							179.47				
Nylon 6/8/12	179.28	178.88	178.73	179.39	179.78	(179.23)	179.99	179.44	179.99	179.60	
Nylon 66	-	-	-	178.19	-	-	-	-	-	-	-
Nylon 66/6	179.29	179.02		178.18	178.49	-	-	-	-	-	-
Nylon 66/12	-	-	-	178.18	-	177.91	179.46	-	-	179.72	
Nylon 6/66/12	179.28	179.01	178.74	178.18	178.48	177.92	179.45	180.03	180.03	179.67	

^aFrom ref. [6].

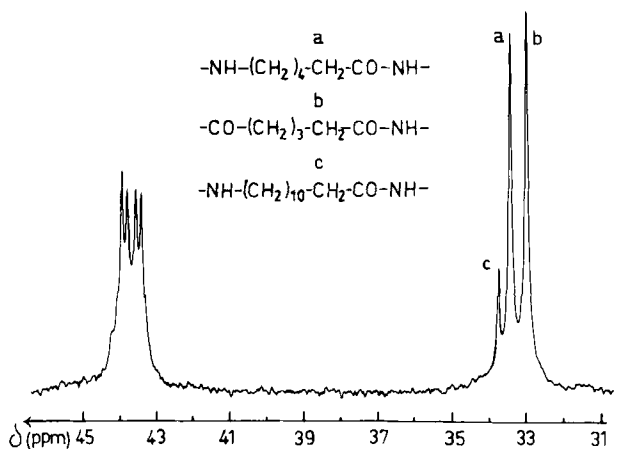


FIG. 3. α - CH_2 and ω - CH_2 signals in the ^{13}C -NMR spectrum (90.5 MHz, FSO_3H) of nylon 6/66/12 prepared from a 1:1:1 mixture of ϵ -caprolactam, AH-salt, and ω -laurinlactam (see Fig. 2B).

of identical amide groups in homopolyamides, binary, or ternary copolyamides are identical within ± 0.025 ppm, if such comparisons are carried out in the same solvent at identical concentration and temperature using the same type of NMR spectrometer.* The shifts of all CO signals are given in Table 1.

Figure 3 shows the signals of methylene C-atoms attached to CO (α -position) and NH groups (ω -position) from the 90.5 MHz spectrum of nylon 6/66/12 of which the CO signals are shown in Fig. 2B. The α -C-signals could easily be assigned by comparison of their shifts with the corresponding homopolyamides [5] and by comparison of their intensity ratio with that of the CO signals (Fig. 2B). While the α -C-signals do not show any sequence effect, the ω - CH_2 signals of the nylon 6 and nylon 66 residues present splittings corresponding to the different amide groups. However, in this case an unambiguous assignment is difficult to achieve, since the peaks are so close together that a comparison with other polyamides gives no clear results. Furthermore, the intensity ratios are influenced by unresolved $-\text{CH}_2$ -signals of the nylon 12 residue. These observations clearly demonstrate that in the case of polyamides the CO signals are most favorable for sequence analysis. In a succeeding paper we shall

*Data for samples measured with an external capillary reference cannot be directly compared with data obtained with iron magnet and superconducting magnet spectrometers.

report, however, that in the case of copolyesters the signals of ester $-O-CH_2-$ groups may be more sensitive to sequence effects than the CO-signals.

Quantitative Evaluation of the NMR Spectra

If signals of (nearly) all different amide groups of a copolyamide are resolved, two kinds of informations can be obtained from a quantitative evaluation of the ^{13}C -NMR spectra: (1) the ratio of monomer units in the isolated copolymer allows one to estimate the relative reactivities of the monomers under the polymerization conditions chosen; (2) the signal intensities of the homogeneous amide bonds (A-A, B-B, C-C) compared with the heterogeneous ones allows one to calculate the average length of the homogeneous blocks. Thus one can determine whether a block copolymer, an alternating sequence or a random copolymer is formed. The following definitions are used for the discussion: A, B, C denote the three different monomer units; I_{AA} , I_{AB} , I_{AC} = intensities of the A-A, A-B, and A-C bond (signals x, x', x'', in Figs. 1 and 2); I_{BB} , I_{BA} , I_{BC} = intensities of the B-B, B-A, and B-C bond (signals y, y', y'' in Figs. 1 and 2); I_{CC} , I_{CA} , I_{CB} = intensities of the C-C, C-A, and C-B bond (signals z, z', z'' in Figs. 1 and 2).

The ratios of monomer units in the copolymer are described as k-values according to Eqs. (1):

$$\begin{aligned} k_{AB} &= A/B = 1/k_{BA} \\ k_{AC} &= A/C = 1/k_{CA} \\ k_{BC} &= B/C = 1/k_{CB} \end{aligned} \quad (1)$$

The ratio of monomer units in a copolymer is given by the concentration of monomers in the reaction mixture if the polymerization is quantitative. If not, the ratio also depends on the reactivity of the monomers and must be calculated from signal intensities or by means of other methods.

For such a calculation all signals may be used that fulfill two conditions. (1) The signal must stem from structurally identical groups in the different monomer units as is the case for $CO-\alpha-CH_2-$ and $\omega-CH_2-$ groups in most aliphatic polyamides. Thus the signal intensities are not influenced by different nuclear Overhauser effects or

different segmental motions. (2) The signals of different monomer units must be resolved to such an extent that unambiguous assignment and quantitative evaluation is possible.

In the case of nylon 6/66/12, both CO- and α -CH₂-signals obey these requirements, while the CO- and α -CH₂-signals of nylon 6/8/12 are less resolved. If clearly separated, as shown in Fig. 3, the α -CH₂-signals are advantageous for a quantitative evaluation for two reasons: the absence of splittings provides a better signal to noise ratio, and in the case of the CO signals, the intensities of more peaks must be measured according to Eqs. (2):

$$k_{AB} = (I_{AA} + I_{AB} + I_{AC}) / (I_{BB} + I_{BA} + I_{BC})$$

$$k_{AC} = (I_{AA} + I_{AB} + I_{AC}) / (I_{CC} + I_{CA} + I_{CB})$$

$$k_{BC} = (I_{BB} + I_{BA} + I_{BC}) / (I_{CC} + I_{CA} + I_{CB}) \quad (2)$$

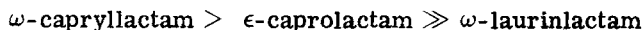
Since all interesting signals are not always well resolved, it is important to keep in mind that in all kinds of copolymers corresponding heterogeneous bonds must be present in equal concentrations. Hence for ternary copolyamides Eqs. (3) must be fulfilled:

$$I_{AB} = I_{BA}$$

$$I_{AC} = I_{CA}$$

$$I_{BC} = I_{CB} \quad (3)$$

Thus from Fig. 1, the following results were obtained: $k_{AB} = 0.85$, $k_{AC} = 6.0$, $k_{BC} = 7.0$; A : B : C = 6 : 7 : 1, indicating the reactivity of the monomers to decrease in the order:



From Fig. 2B and Fig. 3 the following values were estimated: $k_{AB} = 0.9$, $k_{AC} = 4.5$, $k_{BC} = 5.0$; A : B : C = 10 : 9 : 2, indicating the reactivity of the monomers to decrease in the order:

AH-salt > ϵ -caprolactam \gg ω -laurinlactam

These results are in good agreement with those in our investigation on binary copolyamides [5, 6].

In order to calculate the average length of the homogeneous blocks in random copolyamides only the CO signals are useful. The average block length of each monomer unit is given by Eqs. (4):

$$L_A = [I_{AA}/(I_{AB} + I_{AC})] + 1$$

$$L_B = [I_{BB}/(I_{BA} + I_{BC})] + 1$$

$$L_C = [I_{CC}/(I_{CA} + I_{CB})] + 1 \quad (4)$$

Thus the block length of nylon 6 in nylon 6/66/12 prepared from a 1:1:1 monomer mixture (Fig. 2B) is 1.75, while it is 2.75 in the analogous copolyamide prepared from a 2:1:1 monomer mixture (Fig. 2A) and 2.65 in nylon 6/8/12 (Fig. 1). The average block length of nylon 12, on the other hand, is in the range of 1.1-1.2 in all three copolyamides. Since the block length of nylon 8 and nylon 66 is also below 3, we can conclude that all our ternary copolymers possess a structure that is more random than blocklike in character.

Another point of interest is to determine whether the sequence of a copolyamide is the result of a thermodynamically controlled equilibrium caused by transamidation reactions, or a result of a kinetically controlled polymerization. If the sequence is thermodynamically controlled, the intensity ratios of the CO-signals follow Eqs. (5)-(7), since the concentration of every kind of amide groups depends exclusively on the ratio of monomer units under these conditions:

$$I_{AA} = I_{AB}k_{AB} = I_{AC}k_{AC} = I_Bk_{AB}^2 = I_Ck_{AC}^2 \quad (5)$$

$$I_{BB} = I_{BA}k_{BA} = I_{BC}k_{BC} = I_Ak_{BA}^2 = I_Ck_{BC}^2 \quad (6)$$

$$I_{CC} = I_{CA}k_{CA} = I_{CB}k_{CB} = I_Ak_{CA}^2 = I_Bk_{CB}^2 \quad (7)$$

In order to test if a sequence is thermodynamically controlled or not, the signal intensities of homogeneous and heterogeneous bonds must

be compared. If the CO signals of homogeneous bonds are less intense than given by Eqs. (5)-(7), the formation of an alternating sequence is favored. If the signals of homogeneous bonds are more intense, a tendency to form blocks exists, as shown in Fig. 1 in agreement with our previous results from nylon 8/12 [6]. If two or three signals are not well resolved but assigned as for the case for the homogeneous bonds in Fig. 1 (x, y, z), then the sum of the signal intensities may be compared according to Eq. (8) or (9). This investigation revealed that, in contrast to nylon 6/8/12, the copolyamides of Fig. 2A and B possess a thermodynamically controlled primary structure as expected for a condensation at 250°C.

$$\begin{aligned} I_{AA} + I_{BB} &= I_{AB}k_{AB} + I_{BA}k_{BA} \\ &= I_{AB}[k_{AB} + (1/k_{AB})] \end{aligned} \quad (8)$$

$$\begin{aligned} I_{AA} + I_{BB} + I_{CC} &= I_{AB}k_{AB} + I_{BC}k_{BC} + I_{CA}k_{CA} \\ &= I_{AB}[k_{AB} + (1/k_{AB})] + I_{AC}(1/k_{AC}) \\ &= I_{AB}[k_{AB} + (1/k_{AB}) + (k_{AB}/k_{AC})] \end{aligned} \quad (9)$$

A problem which cannot be solved immediately by NMR spectroscopy is the block length distribution within one chain and between different chains of one sample. However, if the sequence of copolyamide is thermodynamically controlled, it is expected that the block length distribution is likewise thermodynamically controlled in analogy with the molecular weight distribution. In other words, the average block length is also the most probable block length in every part of one chain and in all chains of one sample.

Finally it should be pointed out that a quantitative evaluation of ^{13}C -NMR spectra has a limited accuracy for several reasons. If the chain of copolymer is built up of monomer units of a very different structure, their segmental mobility (and hence T_1 's) may be different. In this case, the pulse width and repetition time must be selected to provide accurate intensity ratios. Furthermore, possible differences in the nuclear Overhauser effect must be taken into account. A limiting factor is, of course, the signal-to-noise ratio and the resolution of signals. In most cases only a FT-NMR spectrometer working at a high field strength can provide ^{13}C -NMR spectra of a suitable quality, but no other method can provide the same information in a similarly short time.

REFERENCES

- [1] H. R. Kricheldorf, E. Leppert, and G. Schilling, Makromol. Chem., **175**, 1705 (1974).
- [2] H. R. Kricheldorf, E. Leppert, and G. Schilling, Makromol. Chem., **176**, 81 (1975).
- [3] H. R. Kricheldorf, E. Leppert, and G. Schilling, Makromol. Chem., **176**, 1629 (1975).
- [4] H. R. Kricheldorf and G. Schilling, Makromol. Chem., **177**, 607 (1976).
- [5] H. R. Kricheldorf and R. Mühlhaupt, Angew. Makromol. Chem., **65**, 169 (1977).
- [6] H. R. Kricheldorf and W. E. Hull, J. Polym. Sci. Polym. Chem. Ed., in press.

Accepted by editor July 11, 1977

Received for publication September 12, 1977