Application of f_1 -Decoupled 2D-NMR Methods for Characterizing the Stereochemical Structure of *tert*-Butyl Acrylate Oligomers

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ABSTRACT: The stereochemical structure of *tert*-butyl acrylate (*t*BuA) oligomers prepared in tetrahydrofuran with *tert*-butyl- α -lithioisobutyrate initiation was studied by NMR methods. By combination of various types of one- and two-dimensional NMR methods, resonance lines could be assigned in ^1H and ^{13}C NMR spectra of *t*BuA oligomers (dimer, trimer, tetramer and pentamer) in C_6D_6 solution. The unequivocal assignment of NMR resonance lines to various stereoisomers in the *t*BuA tetramer and pentamer was achieved by means of the f_1 -decoupled COSY experiment. The two isomers present in the sample of *t*BuA tetramer could be identified as *m* (major form) and *r* (minor form) by means of the f_1 -decoupled NOESY experiment; their populations amounted to 0.78 and 0.22, respectively. In the sample of *t*BuA pentamer, the populations of the stereoisomers were $mm:mr:rm=0.635:0.185:0.180$; the population of the *rr* stereoisomer is negligible (does not exceed 0.05). These stereoisomer populations in the *t*BuA pentamer conform to Bernoullian statistics.

KEY WORDS ^1H NMR / ^{13}C NMR / Two-Dimensional (2D) NMR / f_1 -Decoupled 2D NMR / *tert*-Butyl Acrylate Oligomers / Stereochemical Structure /

Janata *et al.*¹ have studied the mechanism and kinetics of *tert*-butyl acrylate (*t*BuA) oligomerization initiated with *tert*-butyl- α -lithioisobutyrate; the individual linear oligomers (dimer, trimer, tetramer, and pentamer) were separated by molecular distillation and

$n=1$: dimer

$n=2$: trimer

$n=3$: tetramer

$n=4$: pentamer

column chromatography. In our preceding communication² we have studied the conformational structure of the *t*BuA dimer and trimer by a combination of infrared and NMR spectroscopy with molecular-mechanics calcu-

lations. The *t*BuA tetramer has two asymmetrical carbons and thus may be expected to appear in the form of two stereoisomers, meso (*m*) and racemo (*r*). Similarly the *t*BuA pentamer, with three asymmetrical carbons, should occur as a mixture of four stereoisomers, *mm*, *mr*, *rm*, and *rr*. The aim of this work was a complete assignment of resonance peaks in ^1H and ^{13}C NMR spectra of *t*BuA oligomers; with *t*BuA tetramer and pentamer, also a complete assignment of the resonance peaks to the various stereoisomers, together with the determination of stereoisomer populations in these samples. To this end we have applied a combination of the one- and two-dimensional techniques of NMR spectroscopy.³

So far, modern NMR methods have been applied in studies of the oligomers of styrene,⁴ and particularly of methyl methacrylate^{5–7}

(MMA). In most cases, however, NMR spectroscopy was used to study directly the individual stereoisomers isolated by preparative high-pressure liquid chromatography. In this way, Ute *et al.*⁷ have assigned the resonance peaks of dimer to octamer for purely isotactic (*m*) and purely syndiotactic (*r*) MMA oligomers. Only Konishi *et al.*⁶ have published an assignment of resonance peaks for MMA trimer and tetramer without previous separation of the individual stereoisomers. In literature^{8–11} the *m/r* assignments for the monomeric sequences in polymers and oligomers were often made on the basis of the nonequivalency of methylene protons. In a given monomeric unit, this nonequivalency was assumed to be larger for *m*-sequences than for *r*-sequences. By means of X-ray analysis of crystalline MMA trimer, Ute *et al.*⁵ have found that this is true for in-chain units, but need not necessarily be true for the methylene protons in chain-end units. Therefore we have applied the f_1 -decoupled NOESY experiment¹² to experimentally determine the configurations of the two stereoisomers in the sample of *t*BuA tetramer.

EXPERIMENTAL

Samples

The preparation and isolation of the studied *t*BuA oligomers is described in ref 1. Also the designation dimer, trimer, tetramer and pentamer follows that of ref 1. The purity of the isolated oligomers was at least 95% (GPC).

NMR Measurements

The samples of various *t*BuA oligomers were dissolved in deuterated benzene to 10% (wt) and 40 or 60% (vol), with hexamethyldisiloxane (HMDS) as internal standard, and measured in 5 mm NMR cells. All further cited chemical shifts in ^1H and ^{13}C spectra are referred to the HMDS signal resonating at 0.05 ppm from TMS in ^1H , and at 2.0 ppm from TMS in ^{13}C spectra. All spectra were measured at room

temperature. The following spectrometers were used: Varian UNITY-500 (499.8 MHz for ^1H and 125.7 MHz for ^{13}C); Bruker AM-400 (400.1 MHz for ^1H and 100.6 MHz for ^{13}C); Bruker AC-300 (300.1 MHz for ^1H and 75.5 MHz for ^{13}C).

For the selective INEPT experiments we used the method as proposed by Bax.¹³ In our case, the selective INEPT measurements were carried out with both delays, $\Delta_1/2$ and $\Delta_2/2$, set to 24 ms; the pulse width of the soft 90° ^1H pulse was set to 7 ms (AM-400) or 16.9 ms (AC-300).

The f_1 -decoupled COSY spectra were obtained with the pulse sequence¹⁴ $90^\circ-t_1/2-180^\circ-(\Delta-t_1/2)-45^\circ$ -acquisition (t_2) with a fixed interval Δ .

The f_1 -decoupled NOESY spectrum was measured with the pulse sequence¹² $90^\circ-t_1/2-180^\circ-(\Delta-t_1/2)-90^\circ-\tau_m-90^\circ$ -acquisition (t_2), with fixed interval Δ and mixing period τ_m .

Heteronuclear NOESY (HOESY) spectra were obtained by the modified HOESY method of Kövér and Batta.¹⁵ The modification consists of a several-fold repetition of a part of the pulse sequence before the reading pulse and detection ("NOE pumping").

In connection with the use of the concentrated solutions of *t*BuA dimer and higher oligomers in C_6D_6 it should be noted that in these solutions the resonances are shifted with respect to their position in the 10% solutions (by up to 0.15 ppm). This can be explained by intermolecular interactions of *t*BuA oligomers with the benzene molecules. With increasing concentration of the solute, the fraction of benzene decreases, and with it also the possibility of these interactions, so that the chemical shifts approach those measured in a more inert solvent (CDCl_3) where the resonance positions are almost independent of concentration.

RESULTS AND DISCUSSION

Dimer and Trimer of *tert*-Butyl Acrylate

The ^1H and ^{13}C NMR spectra of 10% solution of *tert*-butyl acrylate (*t*BuA) dimer in C_6D_6 are shown in Figures 1a and 2a, respectively. For assigning resonance peaks in both these spectra, the selective INEPT experiment proved very useful. With concentrated solutions (60 vol%), individual INEPT spectra can be obtained within minutes. Selective irradiation of the proton CH_2 multiplet at 2.2 ppm produces a spectrum with a single resonance in the carbonyl range (Figure 2b)—this indicates that the irradiated multiplet corresponds to CH_2 -3; the INEPT spectrum exhibits the resonance peak of carbonyl α_2 in the carbonyl range, and the resonances of the methylene carbon CH_2 -2 and of the quaternary carbon C-1 in the aliphatic range. By irradiating the ^1H multiplet at 1.8 ppm (*i.e.*, the group CH_2 -2) we obtain (Figure 2c) a spectrum with resonance peaks of both

Figure 1. 400 MHz ^1H NMR spectra of a 10% solution of *t*BuA dimer (a) and trimer (b) in C_6D_6 .

Figure 2. 75 MHz ^{13}C NMR spectrum of a 60% (vol) solution of *t*BuA dimer in C_6D_6 (a), and selective INEPT spectra (magnitude mode) of the same solution obtained by selective irradiation of protons in the CH_2 multiplet at 2.2 ppm (b) and 1.8 ppm (c).

carbonyl carbons, of the methylene carbon CH₂-3 and of the quaternary carbon C-1, together with a weak band of the methyl carbons bound to C-1.

The two *tert*-butyl bands in the ¹H spectrum could be assigned by means of a HOESY spectrum. From the region of the cross peaks of carbonyl carbons with *tert*-butyl group protons in the HOESY spectrum it could be concluded that the *tert*-butyl peak at lower field in the ¹H spectrum corresponds to *tert*-butyl 5. HOESY spectra also enabled us to assign the poorly resolved resonance peaks of the quaternary carbons 4 and 5 and the methyl carbons of *tert*-butyl groups in the ¹³C spectrum. The complete assignment of ¹H and ¹³C resonance peaks for the *t*BuA dimer is shown in Table I.

The ¹H NMR spectrum of a 10% solution of *t*BuA trimer in C₆D₆ is shown in Figure 1b. Because of the presence of the asymmetric carbon CH-3, the methyl groups bound to carbon C-1 are nonequivalent, and the corresponding resonance peaks are resolved in

both ¹H and ¹³C spectra. The methylene and methine multiplets could be unequivocally assigned by means of the COSY-45 experiments³ (Figure 3).

With a known assignment of resonance peaks in the ¹H NMR spectrum, it is possible to assign the directly interacting (*via* ¹J_{CH})

Table I. Assignment of resonances in ¹³C and ¹H NMR spectra of *t*BuA dimer in C₆D₆

Group	Chemical shifts (ppm to HMDS)	
	¹³ C	¹ H
CH ₃ bound to carbon 1	23.1	0.95
CH ₃ bound to carbon 4	25.9	1.20
CH ₃ bound to carbon 5	26.1	1.27
C-1	40.3	—
CH ₂ -2	33.7	1.79–1.86
CH ₂ -3	29.8	2.14–2.20
C-4	77.5	—
C-5	77.4	—
α ₁	174.0	—
α ₂	170.4	—

Figure 3. 300 MHz COSY-45 spectrum of a 10% solution of *t*BuA trimer in C₆D₆. The ⁴J_{HH} connectivities discussed in the text are enclosed by solid lines.

Table II. Assignment of resonances in ^{13}C and ^1H NMR spectra of *t*BuA trimer in C_6D_6

Group	Chemical shifts (ppm to HMDS)	
	^{13}C	^1H
CH_3 bound to carbon 1	25.1; 22.1	1.03; 1.11
CH_3 bound to carbon 6	26.1	1.27
CH_3 bound to carbon 7	26.0	1.24
CH_3 bound to carbon 8	25.9	1.27
C-1	41.0 ₅	—
CH_2 -2	40.4	1.60—1.66; 1.95—2.02
CH-3	41.0	2.35—2.43
CH_2 -4	28.3	1.79—1.87
CH_2 -5	31.1	2.12—2.27
C-6	77.6	—
C-7	77.8	—
C-8	77.6 ₅	—
α_1	174.2	—
α_2	173.2	—
α_3	169.8	—

carbons by means of the HETCOR experiment. The carbon peaks in the carbonyl range were again successfully assigned by means of a series of several selective INEPT experiments. Similarly as in the case of the *t*BuA dimer, the HOESY experiment was applied for assigning the two *tert*-butyl bands in the ^1H spectrum. The HOESY spectrum also indicates that the quaternary carbons 6 and 8 produce in the ^{13}C spectrum a pair of peaks resonating at higher field, while the quaternary carbon 7 resonates at lower field. The complete assignment of ^{13}C and ^1H resonance peaks of *t*BuA trimer is shown in Table II.

The COSY spectrum of *t*BuA trimer (Figure 3) exhibits, besides others, also a cross peak indicating a four-bond interaction (W pathway coupling) between one of the methyls bound to carbon C-1 (1.11 ppm) and one of the two non-equivalent protons of group CH_2 -2 (1.60—1.66 ppm) (a similar cross peak is observed in COSY spectra of *t*BuA tetramer and pentamer). This methyl and proton are thus expected to lie in the plane passing through carbons 1 and 2, and should be in mutual

trans orientation. This conclusion is supported by the previously observed temperature dependence of the coupling constant $^3J_{\text{CH}}$ between the α_1 carbonyl carbon and the 2-methylene protons in *t*BuA dimer, as well as by MM2 molecular mechanics computations.² These four-bond planar W pathway couplings have been often observed in saturated cyclic systems, but in acyclic systems are rather rare. Johns *et al.*¹⁶ made use of this interaction for determining the preferred conformer of methyl methacrylate dimer, and a similar interaction was observed between one of the two nonequivalent CH_2 protons and the α -methyl protons in isotactic PMMA.¹⁷

Tetramer of *tert*-Butyl Acrylate

Assignment of ^1H and ^{13}C NMR Bands

The ^1H NMR spectrum of a 10% solution of *t*BuA tetramer in C_6D_6 is shown in Figure 4a. From the expanded carbonyl region of the ^{13}C NMR spectrum of the same sample (Figure 4b) it is evident that the sample consists of two isomers. It may be expected that the two isomers will differ by the mutual orientation of the two *tert*-butyl substituents bound to the groups CH-3 and CH-5. This mutual orientation of the two substituents should correspond to the configuration occurring in the *racemic* or *meso* diads of the polymer. From the ratio of band intensities in the ^{13}C NMR spectrum, the population ratio of the two stereoisomers in the sample can be estimated as roughly 4 : 1. Such difference in population is favourable for identifying the ^{13}C resonance peaks corresponding to the individual isomers.

The COSY-45 spectrum of *t*BuA tetramer is shown in Figure 5. Owing to the appearance of a complicated multiplet at 2.4 ppm, caused by overlap of the CH-3 and CH-5 methine ^1H

Figure 4. 400 MHz ^1H NMR spectrum of a 10% solution of *t*BuA tetramer in C_6D_6 (a), and the range of carbonyl resonances in a 100 MHz ^{13}C NMR spectrum of the same solution (b).

resonances of the two isomers (to be proved in the following by the HETCOR spectrum of the tetramer), resonance assignment by means of this COSY-45 spectrum is not unambiguous.

For a clearcut assignment of the proton resonances to the two isomers, the f_1 -decoupled COSY experiment¹⁴ was found as very effective. In our opinion, this experiment is unjustly neglected in practical applications: although it is handicapped, similarly as other f_1 -decoupled experiments, by the occurrence of artifacts (*e.g.*, Hikichi *et al.*¹⁸ describe that along a line with a slope of $-1/2$ there appear ghost peaks accompanied by ghost cross peaks due to fast relaxation recovery for a constant period Δ) and sensitivity to deviations from the weak coupling limit (in strongly coupled systems artifacts appears, as shown, *e.g.*, by

Bax¹⁹), the resulting spectrum is nevertheless often very informative, and this is also true in our case. The f_1 -decoupled COSY spectrum of *t*BuA tetramer (40% solution in C_6D_6) is shown in Figure 6.

The cross peak between the methyl bound to carbon C-1 (resonating at 1.13 ppm) and one of the nonequivalent protons of the group CH_2 -2 (observed and discussed already with the *t*BuA trimer) identifies the resonance of this proton in the spectrum (1.62–1.69 ppm). As in the proton spectrum, the methyls bound to C-1 are equivalent, it must be assumed that also for the minor isomer a similar interaction with one of the nonequivalent protons should occur, and thus also the position of the nonequivalent proton that is coupled to one methyl of the pair bound to carbon C-1 should be identical for the two isomers. This corresponds to the observation that this proton shows a stronger cross peak with the CH range (2.38–2.46 ppm) and with the other nonequivalent proton (2.0–2.06 ppm) and a weaker cross peak again with the CH range, and with the other nonequivalent proton (1.90–1.96 ppm). In this connection it is necessary to inspect the CH range where three resonances are clearly shown. The mentioned nonequivalent proton produces a stronger cross peak with the left methine band (at lower field) and a weaker cross peak with the central methine band. In this way the resonances of the nonequivalent protons of the group CH_2 -2 and of methine 3 can be localized for both isomers in the spectrum of their mixture (Table III). Now it is necessary to find in the low-field region of the f_1 -decoupled COSY spectrum—the range of the methine resonance cross peaks—a further pair of signals exhibiting mutual coupling and a cross peak with the left methine band (CH-3 of the major isomer). It is evident that this applies to the pair (in this spectrum at 1.99 and 1.46 ppm) with a cross peak involving by its length both the left, and the central methine bands. This resonance pair must necessarily be assigned to the non-

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Figure 5. Section from a 400 MHz COSY-45 spectrum of a 40% (vol) solution of *t*BuA tetramer in C_6D_6 .

Figure 6. 500 MHz f_1 -decoupled COSY spectrum of a 40% (vol) solution of *t*BuA tetramer in C_6D_6 . Fixed interval Δ was 0.217 s. The solid lines in the spectrum indicate the peak connectivities for the major isomer (*meso*). The numbers represent the corresponding CH or CH_2 groups in the structural formula given in the text.

Table III. Assignment of resonances in ^{13}C and ^1H NMR spectra of *t*BuA tetramer in C_6D_6

Group	Chemical shifts ^a (ppm to HMDS)			
	<i>meso</i> Isomer		<i>racemo</i> Isomer	
	^{13}C	^1H	^{13}C	^1H
CH_3 bound to C-1	22.3; 22.9	1.13; 1.06	22.3; 25.1	1.13; 1.06
CH_3 in <i>tert</i> -butyl	26.0—26.1	1.20—1.35	26.0—26.1	1.20—1.35
Quart. C in <i>tert</i> -butyl	77.6—78.0	—	77.6—78.0	—
C-1	41.0	—	41.0 _s	—
CH_2 -2	40.3	1.62—1.69; 2.02—2.10	41.8	1.62—1.69; 1.92—1.99
CH-3	39.6	2.43—2.50	40.1	2.40—2.48
CH_2 -4	35.5	1.45—1.53; 2.00—2.08	35.8	1.55—1.63; 1.71—1.78
CH-5	41.6 _s	2.40—2.48	41.7	2.37—2.43
CH_2 -6	25.6	1.82—1.93	27.2	1.71—1.80
CH_2 -7	31.3	2.12—2.26	31.0	2.09—2.17
α_1	174.2	—	174.1 _s	—
α_2	173.1	—	173.4	—
α_3	172.1	—	172.2	—
α_4	169.7 _s	—	169.6 _s	—

^a ^1H chemical shifts from f_1 -decoupled NOESY spectra of a 2% solution of *t*BuA tetramer in C_6D_6 .

equivalent proton pair of the group CH_2 -4 in the major isomer, and the central methine band to the CH-5 methine, likewise in the major isomer. From this it also follows that the resonances of methine 3 in the minor and methine 5 in the major isomer overlap in this central methine band, and that the right methine band necessarily corresponds to methine 5 of the minor isomer. In the spectrum (Figure 6), the strong coupling of the end-standing groups CH_2 -6 and CH_2 -7 is evident at first sight (the corresponding signals are surrounded by artifacts), so that the resonances of the end-standing group CH_2 -7 in the major and minor isomers must be assigned to the regions 2.12—2.26 ppm and 2.13—2.18 ppm, respectively. The resonance positions of the CH_2 -6 groups in the two isomers exhibit a slightly larger difference (here 1.80—1.92 ppm for the major, and about 1.7 ppm for the minor isomer). In this way, it is possible to assign, by means of the f_1 -decoupled COSY spectrum, essentially all proton resonances of the two isomers.

The correctness of our assignment was also confirmed by the HETCOR spectrum, revealing the mutual position of the pairs of nonequivalent protons of the groups CH_2 -2 and CH_2 -4 in both isomers. For the assignment of carbon resonances in the carbonyl range of the two isomers, the COLOC experiment³ was applied, adjusted for transfer over $J_{\text{CH}} = 12$ Hz, together with a series of selective INEPT spectra. The assignment of carbonyl resonances is also borne out by the HOESY spectrum, the carbonyl range of which is shown in Figure 7.

The assignments of ^1H and ^{13}C NMR resonances of the major and minor isomers of *t*BuA tetramer are summarized in Table III.

Configuration of the Major and Minor Isomers

i) The HETCOR spectrum clearly indicates that for the major isomer, the chemical shift difference of the nonequivalent protons in the group CH_2 -4 is larger than for the minor isomer. If our “monomeric unit”— $^4\text{CH}_2$ — ^5CH —is regarded as an in-chain unit, this would indicate that the major isomer has the carboxyl

Figure 7. Section from a 75 MHz ^{13}C - ^1H HOESY spectrum of a 60% (vol) solution of *t*BuA tetramer in C_6D_6 , measured by the modified HOESY method (3×1.5 s prior to detection).

groups α_2 and α_3 in *m*-configuration, and the minor isomer in *r*-configuration.

ii) If the configurations of the two isomers of *t*BuA are schematically represented in *tt* conformation, which in both cases has been shown by molecular mechanics calculations (MM2)² to be favoured by energy, we see that in *meso* configuration the protons of methine groups 3 and 5 are nearer to the same proton of the nonequivalent pair of CH_2 -4, whereas in case of the *racemic* configuration of substituents, each of the methine protons 3 and 5 is nearer to a different proton of the pair CH_2 -4. To test this difference, a f_1 -decoupled NOESY experiment was run with a 2% degassed solution of the tetramer. The obtained spectrum is shown in Figure 8.

If we draw slices through the f_1 -decoupled NOESY spectrum parallel to the f_1 axis so as to always pass predominantly through one of the three methine signals, we can make conclusions on the relative distance of the protons from the given methine. On drawing the slice through the left methine band at 2.49 ppm (Figure 9a), we can assume that the intensity of the signals will be a measure of the distance of nearby protons to the methine 3 proton of the major isomer. From the slice it is evident that of the two nonequivalent protons of group CH_2 -4 in the major isomer (1.49 and 2.04 ppm), that at 2.04 is nearer to this methine (the same result is obtained from the slices at 2.47 and 2.48 ppm). If we draw the slice at 2.44 ppm (Figure 9b), we can assume

Figure 8. Section from a 500 MHz, f_1 -decoupled NOESY spectrum of a 2% solution of *t*BuA tetramer in C_6D_6 . Fixed interval Δ was 0.15 s, mixing period 0.1 s. The solid lines in the spectrum indicate the peak connectivities for the major isomer (*meso*). The numbers represent the corresponding CH or CH_2 groups in the structural formula given in the text.

Figure 9. Slices of f_1 -decoupled NOESY spectrum from Fig. 8, parallel to the f_1 axis at 2.49 ppm (a), 2.44 ppm (b), and 2.40 ppm (c). The positions of the two nonequivalent CH_2 -4 protons of the major (*m*) and the minor (*r*) isomers are indicated by arrows.

that the intensity of the signals will be a measure of the distance of nearby protons from the methine 5 proton of the major isomer and from the methine 3 proton of the minor isomer. This slice indicates that once more the proton resonating at 2.04 ppm is nearer to this methine than the proton resonating at 1.49 ppm (the same result is obtained from slices at 2.46 and 2.43 ppm). This means that both methines of the major isomer are nearer to the same proton of the nonequivalent pair of group CH_2 -4 (and farther from the other proton of this pair), and therefore that the major isomer corresponds to *m*-configuration. In the same slice we can also follow the relative distances of the protons in the minor isomer to methine 3 of the minor isomer. The nonequivalent protons of group CH_2 -4 of the minor isomer appear in this slice at 1.74 and 1.59 ppm. From the slice it is evident that the proton resonating at 1.74 ppm is nearer

to methine 3 of the minor isomer than the proton resonating at 1.59 ppm (the same result follows also from the slices at 2.46 and 2.43 ppm). By drawing the slice at 2.40 ppm we can test the distance of protons to methine 5 of the minor isomer. This slice indicates (Figure 9c) that the proton at 1.59 ppm is nearer to this methine than the proton at 1.74 ppm (the same result also follows from the slice at 2.41 ppm, in the slice at 2.39 ppm the peak at 1.74 ppm was overlapped by large artifacts from the crosspeak of methine and group CH₂-6 of the minor isomer). From these slices it can be concluded that the minor isomer corresponds to *racemic* configuration.

iii) Large effort has been paid to experimental verification of isomer configuration by HOESY spectroscopy. Although its very low sensitivity has been improved by the modification of the basic pulse sequence according to Kövér and Batta,¹⁵ it still remained too low for our purpose. In the HOESY spectrum (Figure 7) it is possible to draw slices (parallel to the axis f_1) through the carbonyl peaks and by means of signal intensities in each slice to estimate the relative distances of protons from this carbonyl. For our assignment of isomer configurations, carbonyls α_2 and α_3 of both isomers are important. It may be expected that in the *m*-isomer, both carbonyls will be nearer to the same proton of the nonequivalent pair of group CH₂-4, whereas in *r*-configuration, each carbonyl should be nearer to a different proton of this pair. Unfortunately, slices through carbonyl α_2 and α_3 signals of the major isomer cannot be used, because owing to poor resolution in the f_1 axis, overlap is expected to occur between one of the group CH₂-2 and one of the group CH₂-4 nonequivalent protons, and between the other CH₂-4 proton and the *tert*-butyl cross peak. From the slices through the carbonyl signals of the minor isomer in this spectrum it may be stated that in spite of very low resolution (37 increments—a required resolution would prohibitively prolong the already long experiment), the obtained slices

are not at variance with the *r*-configuration of the minor isomer. In concentrated solution, the nonequivalent protons of group CH₂-4 of the minor isomer resonate at 1.55 and 1.65 ppm, and these slices exhibit reversed relative peak intensities in these regions. The same can be stated about slices through the signals of minor isomer carbonyls in a HOESY spectrum obtained under somewhat different conditions (three times repeated sequence, with a mixing period of 2 s before detection).

All the above discussed circumstances lead us to the conclusion that the major isomer is of *meso*-, and the minor isomer of *racemic* configuration. In order to quantitatively determine the populations of both isomers in the sample, we measured the ¹³C spectrum of a 40% (by volume) solution of *t*BuA tetramer in C₆D₆ without NOE (¹H decoupling only during detection) and with a delay of 50 s between end of detection and next pulse. By integration of carbonyl α_2 peaks (which were best resolved), the populations of the major *m*-isomer and minor *r*-isomer were found to be equal to 0.78 and 0.22, respectively.

Pentamer of *tert*-Butyl-Acrylate

The ¹H NMR spectrum of a 10% solution of *t*BuA pentamer in C₆D₆ is shown in Figure 10. From our study of *t*BuA tetramer it can be expected that the sample of pentamer will be composed of four isomers, corresponding to the configuration of the three *tert*-butyl substituents (α_2 , α_3 , and α_4): *mm*, *mr*, *rm*, and *rr*, with the *mm* configuration dominating. The populations of *mr* and *rm* configurations are expected to be lower and similar (or equal in case of Bernoulli statistics), while the population of *rr* configuration should be very small.

Because of serious band overlap, a detailed resonance assignment by means of a classical

Figure 10. 400 MHz ^1H NMR spectrum of a 10% solution of *t*BuA pentamer in C_6D_6 (a), and the range of carbonyl resonances in 100 MHz ^{13}C NMR spectrum of the same solution.

COSY spectrum (Figure 11) is not possible even for the most populated isomer. Therefore an f_1 -decoupled COSY spectrum was again measured (Figure 12). By means of this spectrum it was possible to assign all proton resonances of the *mm* isomer. The relative positions of pairs of nonequivalent protons found by analysis of the f_1 -decoupled COSY spectrum correspond to the positions of these protons in the HETCOR spectrum (Figure 13), confirming the correctness of our assignment on one hand, and defining the positions of the ^{13}C resonances of these methylenes on the other hand. The three methine bands of this isomer are well resolved, and this is useful for the assignment of the corresponding ^{13}C methine resonances. According to the f_1 -de-

coupled COSY spectrum, the central methine band corresponds to methine 3, the low-field one to methine 5, and the high-field one to methine 7. From the HETCOR spectrum we can then easily assign the ^{13}C resonance at 39.8 ppm to methine 3, that at 40.4 ppm to methine 5, and that at 41.8 ppm to methine 7.

To complete the assignment of the *mm* isomer, we still have to find its carbonyl resonances. In the ^{13}C carbonyl range (Figure 10b), we can easily identify five strong peaks of the *mm* isomer. These can again be assigned by means of selective INEPT spectra. From their combination, an unequivocal assignment of the carbonyl bands of the *mm* isomer can be obtained. However, assignment by means of a COLOC spectrum is more straightforward. From that it is evident that carbonyl α_1 (coupled to methyls on carbon C-1) resonates at 174.2 ppm, and carbonyl α_5 (coupled to methylene group 8) at 169.8 ppm. Carbonyls α_2 , α_3 , and α_4 can be assigned by means of the cross peaks of these carbonyls with methine protons. As in the ^1H NMR spectrum methine 3 resonates between the remaining two methine bands, the ^{13}C resonance of carbonyl α_2 must lie at 173.2 ppm. The proton resonance of methine 5 lies at lower field, therefore carbonyl α_3 corresponds to the peak at 172 ppm and carbonyl α_4 to that at 172.1 ppm. The large chemical shift difference of nonequivalent protons in the groups CH_2 -4 and CH_2 -6 is to be expected in the *mm* configuration.

Resonance assignment for the less populated *mr* and *rm* isomers of *t*BuA is much more complicated. Owing to the practically equal resonance intensities of these two isomers, the resonances cannot be grouped according to their correspondence to one of the isomers. From an APT spectrum²⁰ we can easily determine the ^{13}C resonance frequencies of the six methine and ten methylene signals of these two isomers. The HETCOR spectrum (Figure 13) further indicates that six of these ten methylenes have nonequivalent protons. The

Figure 11. Section from a 400 MHz COSY-45 spectrum of a 40% (vol) solution of *t*BuA pentamer in C_6D_6 .

relative positions of these nonequivalent pairs can then be used for their localization in the f_1 -decoupled COSY spectrum, by means of which even the resonances of the two less populated isomers can be assigned in a manner analogous to the *mm* isomer. For the assignment of the carbonyl resonances of these two isomers, a combination of several selective INEPT spectra proved to be more suitable, mainly owing to their better resolution. The configurations of the two less populated isomers (*mr* and *rm*) were determined on the basis of chemical shift differences between nonequivalent protons of the groups CH_2-4 and CH_2-6 (this difference is expected to be substantially larger for the *m*-configuration). Owing to the very low population of the configurational isomer *rr* in the mixture of *t*BuA pentamer isomers, and to overlap of its resonances with those of the more populated isomers, an assignment of its 1H and ^{13}C resonances was not possible.

The assignment of 1H and ^{13}C resonances

of *mm*, *mr*, and *rm* isomers of *t*BuA pentamer is summarized in Table IV.

To quantitatively determine the populations of configurational isomers *mm*, *mr*, and *rm* in the sample of *t*BuA pentamer, the ^{13}C NMR spectrum of its 40% (vol) solution in C_6D_6 was measured without NOE and with a delay of 50 s between end of detection and further pulse. By integration of α_2 carbonyl resonances of the isomers *mm*, *mr*, and *rm*, the ratio of the corresponding band areas was found to be equal to 0.635:0.185:0.180. This ratio is somewhat affected by the presence of the α_2 peak of isomer *rr* (probably overlapping the α_2 resonance of the *mm* isomer), with an expected population of 0.05 (from the populations of *m* and *r* isomers in *t*BuA tetramer and assumed operation of Bernoulli statistics [$(rr) = (1 - P_m)^2$; $P_m = 0.78$]). The similarly calculated expected populations of the more abundant isomers [$(mm) = P_m^2$; $(mr) = (rm) = P_m(1 - P_m)$], *mm*:*mr*:*rm* = 0.61:0.17:0.17, are in very good agreement with the measured values. Therefore

Figure 12. Section from a 500 MHz f_1 -decoupled COSY spectrum of a 10% solution of *t*BuA pentamer in C_6D_6 . Fixed interval Δ was 0.208 s. The solid lines in the spectrum indicate the peak connectivities for the major isomer (*mm*). The numbers represent the corresponding CH or CH_2 groups in the structural formula given in the text.

it is possible to state that propagation of *t*BuA oligomerization under the given conditions is governed by Bernoulli statistics. This result is in accord with the finding that also PtBuA samples prepared by group transfer and anionic polymerization obey Bernoulli statistics.²¹

CONCLUSIONS

By means of modern methods of NMR spectroscopy, resonances in 1H and ^{13}C NMR spectra of *t*BuA dimer and trimer were assigned. Analysis of the spectra of *t*BuA tetramer revealed that the sample consists of two isomers—*m* and *r*. For resonance assignment in the NMR spectrum of the tetramer,

Figure 13. 400 MHz ^{13}C - ^1H HETCOR spectrum of a 40% (vol) solution of *t*BuA pentamer in C_6D_6 . The peak assignment is indicated for the major (*mm*) isomer.

the f_1 -decoupled COSY experiment was found as very effective. The configuration of the two isomers was experimentally determined by means of an f_1 -decoupled NOESY experiment, based on the difference in the distance of the two nonequivalent protons of group CH_2 -4 to the methine protons CH-3 and CH-5; the major isomer was found to be of *meso*, and the minor isomer of *racemic* configuration. The chemical shift difference of nonequivalent protons in the respective units (CH_2 -4) was larger for the *m*-isomer than for the *r*-isomer. The populations of the two isomers in the tetramer sample, as determined from the integrated intensities of α_2 carbonyl resonances, were 0.78 (*m*) and 0.22 (*r*).

Of the expected four isomers of *t*BuA pentamer (*mm*, *mr*, *rm*, and *rr*), the resonances of the three more populated isomers (*mm*, *mr*, and *rm*) could be assigned, mainly by means of the f_1 -decoupled COSY experiment. The

configurations of these isomers were determined on the basis of chemical shift differences between nonequivalent protons in the corresponding methylene groups. The populations of these isomers (*mm*:*mr*:*rm* = 0.635:0.185:0.180) correspond to values calculated from the known populations of configurational isomers in *t*BuA tetramer and assumed operation of Bernoulli statistics. The similarly calculated population of the unassigned *rr* isomer amounts to 0.05 and approaches the impurity level.

In the spectra of *t*BuA trimer, tetramer and pentamer, a scalar four-bond spin-spin coupling ("W coupling pathway") was detected between one of the methyls bound on carbon 1 and one of the pair of nonequivalent protons of group CH_2 -2. For this four-bond planar W coupling pathway to occur, the respective nonequivalent proton of group CH_2 -2 should be in *trans* position to the methyl carbon 1;

Table IV. Assignment of resonances in ^{13}C and ^1H NMR spectra of *t*BuA pentamer in C_6D_6

Group	Chemical shifts ^a (ppm to HMDS)					
	<i>mm</i> Isomer		<i>mr</i> Isomer		<i>rm</i> Isomer	
	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H
CH_3 bound to C-1	24.8; 22.3 ₅	1.07; 1.14	24.7; 22.4 ₅	1.07; 1.14	25.1; 22.3	1.06; 1.13
CH_3 in <i>tert</i> -butyl	26.0—26.1	1.24—1.38	26.0—26.1	1.24—1.38	26.0—26.1	1.24—1.38
Quart. C in <i>tert</i> -butyl	77.6—78.0	—	77.6—78.0	—	77.6—78.0	—
C-1	40.9 ₅	—	40.9	—	41.1	—
CH_2 -2	40.1	1.66—1.73; 2.07—2.15	40.3	1.65—1.74; 2.06—2.15	41.9	1.64—1.70; 1.94—2.00
CH-3	39.8	2.45—2.52	39.6	2.46—2.53	40.0 ₅	2.44—2.52
CH_2 -4	35.6	1.51—1.58; 2.04—2.11	36.8	1.46—1.53; 2.04—2.10	35.9	1.64—1.71; 1.72—1.79
CH-5	40.4	2.52—2.58	40.8	2.48—2.55	40.4	2.43—2.50
CH_2 -6	33.1	1.56—1.63; 2.06—2.13	33.5	1.59—1.66; 1.76—1.84	34.5	1.38—1.46; 2.00—2.07
CH-7	41.8 ₅	2.38—2.46	41.9 ₅	2.42—2.51	41.5	2.39—2.46
CH_2 -8	25.6	1.84—1.90	27.1	1.68—1.76	25.8	1.79—1.85
CH_2 -9	31.3	2.18—2.26	31.1	2.12—2.18	31.2	2.13—2.18
α_1	174.2	—	174.2	—	174.1 ₅	—
α_2	173.2	—	173.0	—	173.4	—
α_3	172.0	—	172.3	—	172.1 ₅	—
α_4	172.1	—	172.2	—	171.9	—
α_5	169.8	—	169.7	—	169.8	—

^a ^1H chemical shifts from f_1 -decoupled COSY spectra of a 10% solution of *t*BuA pentamer in C_6D_6 .

this is in agreement with the results of our previous communication.²

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