Oligomerization of Vinyl Monomers. 24. Anionic Oligomerization of Methyl Methacrylate in Tetrahydrofuran and Toluene

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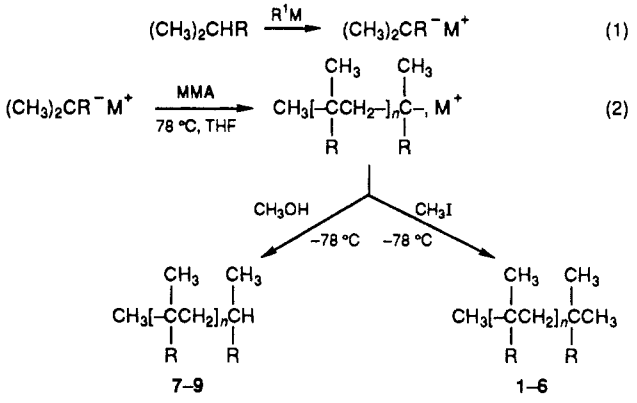
ABSTRACT: The anionic oligomerization of methyl methacrylate initiated by lithium and sodium salts of alkyl isobutyrates carried out in THF, toluene, and THF/toluene was terminated by methylation (CH_3I) or protonation (CH_3OH), and the stereochemistry of oligomerization was determined by NMR and GC. Detailed stereochemical analysis of tetramers, pentamers, and hexamers forms a basis for unambiguous assignment of the ^{13}C NMR spectrum of $^{13}CH_3$ end-labeled PMMA in terms of the stereochemistry of the three preceding diads. Gas chromatographic analysis of the distribution of oligomer stereoisomers formed in THF at −78 °C in the presence of Li ion is in general agreement with the stereochemistry of PMMA prepared under these conditions. The distribution of stereoisomers of the pentamer and hexamer prepared at −20 °C in THF/toluene in the presence of Na ion indicates that the anions flanked by isotactic triads preferentially undergo Claisen cyclization.

Introduction

The oligomerization of vinyl monomers is of interest both from the point of view of obtaining polymer models and from a mechanistic perspective.[1-6] The availability of models is also important for the unambiguous assignment of the stereochemistry of the chain end obtained from NMR studies of labeled end groups.[7] We now report in more detail on the synthesis, isolation, and characterization by GC and NMR of oligomers of MMA prepared as shown in eqs 1 and 2.



R = $-C(O)OCH_3$, R^1M = $(i\text{-}Pr)_2NLi$ or $(Me_3Si)_2NNa$

1, $n = 1$; **2**, $n = 2$; **3**, $n = 3$; **4**, $n = 4$; **5**, $n = 5$; **6**, $n = 6$; **7**, $n = 1$; **8**, $n = 2$; **9**, $n = 3$

Results and Discussion

The oligomers are prepared as previously reported by slow (1–2 h) in vacuo distillation of MMA onto a cold (−78 °C) solution of lithio- or sodioisobutyrate in THF or THF/toluene followed by reaction with CH_3I or CH_3OH. The methylation is slow (several hours at −78 °C), and generally a 4–10 times excess of CH_3I is used. After the usual workup (see the Experimental Section), the oligomers are separated by preparative liquid chromatography by using CH_3CN–*n*-BuCl.[3] For the Li/THF system (sample A) the reaction (at −78 °C) was relatively clean and the occurrence of side reactions was minimal. For sample B prepared in THF/toluene at −20 °C in the presence of Na ion, the occurrence of Claisen condensation was prominent, leading especially to the formation of cyclic products[7] in about 45% yield. These cyclic oligomers also contain configurational isomers, which were difficult to separate completely from the linear oligomers. Although the complete separation of individual isomers was not possible, the use of liquid chromatography led to samples enriched in particular stereoisomers. The identification of these individual isomers was then readily carried out by a combination of ^1H and ^{13}C NMR and GC and comparison with analogous oligomers such as the oligomers based upon 2-isopropenylpyridine. Analytical gas chromatography using capillary columns was especially useful since in this case the stereoisomers were better resolved than by LC. The elution volume was shown to depend upon the meso content of the oligomers. Thus, oligomers with a higher meso content were eluted earlier. The same trend, although less dramatic, was evident from the LC chromatograms. Similar results were obtained for the MMA oligomers derived from the corresponding triphenylmethyl methacrylate oligomers, which were in turn prepared by using fluorenyllithium(−) spartein as initiator.[4a] The correlation between GC and LC retention and stereochemistry was found to be opposite for the oligomers of 2- and 4-vinylpyridine and styrene where the syndiotactic oligomers eluted first.[1,2] Gas chromatography also confirmed that the distribution of stereoisomers was the same in the crude reaction product and in the LC oligomer fractions. Thus the workup did not affect the distribution of stereoisomers.

Stereochemistry of Trimer 2. This oligomer is of interest since, the absence of an asymmetric center notwithstanding, the terminal methyl groups are diastereotopic.[3,9] This is readily apparent from the ^1H and ^{13}C NMR spectra of **2** (Figures 1 and 2) where three absorptions are observed corresponding to the two pairs of external diastereotopic methyls and the internal methyl. The assignment of the up- and downfield terminal methyls of **2** as due to the methyl groups in the pro-m and pro-r positions, respectively,[8] is based on that of the diastereotopic methyls of the analogous trimer and higher oligomers of 2-isopropenyl(2-IP)pyridine.[2,9] The correspondence between the oligomers of MMA and 2-IP is supported by the observation that, upon methylation ($^{13}CH_3I$) of the precursor anions, the dominant $^{13}CH_3$ group corresponds to the downfield absorption (see below).[9] The upfield shift of the pro-m methyl in the case of the 2-IP

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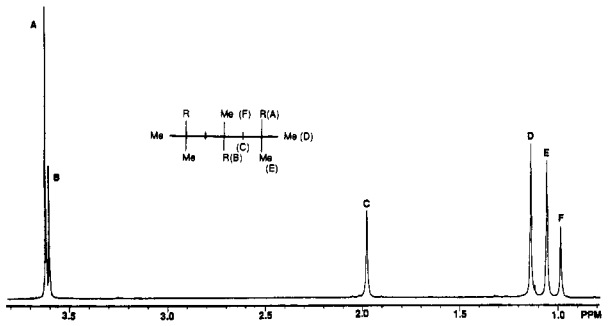


Figure 1. ^1H NMR (200-MHz) spectrum of trimer **2** in $CDCl_3$ at 25 °C.

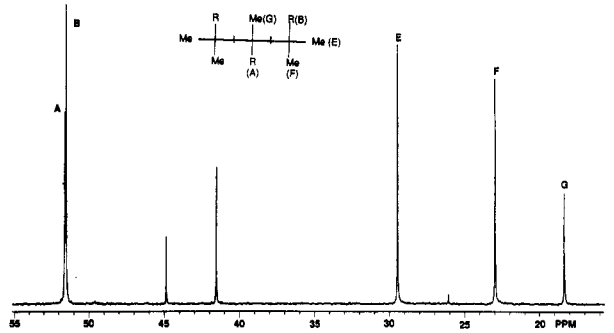


Figure 2. ^{13}C NMR 50-MHz spectrum of trimer **2** in 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2) at 25 °C.

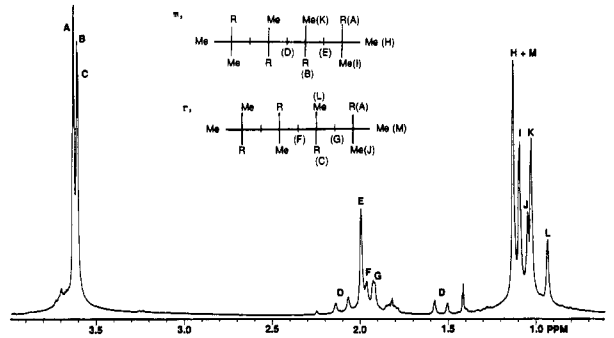


Figure 3. ^1H 200-MHz NMR spectrum of tetramer **3** (meso/racemic = 3/1) in TCE-d_2 at 25 °C.

oligomers was shown to be correlated with an all-trans conformation demonstrated for the syndiotactic 2-IP tetramer by X-ray analysis, with the pro-m methyl being shielded by the penultimate 2-pyridine ring.[2] A similar rationalization in the present case seems reasonable. The central methyl of **2**, as in the case of the 2-IP trimer, is shifted further upfield as a result of diamagnetic shielding by two ester or pyridine groups. The protonated trimer **7** isolated from oligomer sample C was determined by GC to be a 64/36 mixture of the "racemic" and "meso" stereoisomers, respectively. This was confirmed by ^1H and ^{13}C NMR analysis.

The stereochemistry of tetramer 3 was determined from the ^1H and ^{13}C NMR spectra of a 3/1 (m/r) mixture isolated by liquid chromatography from sample B. The ^1H spectrum of this sample (Figure 3) in dichloroethane-d_2 clearly shows the AB quartet due to the two nonequivalent central geminal protons. This feature, of course, is well-known in isotactic PMMA. Interestingly, the external CH_2, although having nonequivalent protons, in both isomers appears as a singlet. Likewise, the central methylene of the racemic isomer is a singlet, as is the corresponding CH_2 absorption of the syndiotactic polymer. As in the trimer, the nonequivalence of the diastereotopic terminal methyls is quite pronounced in both the

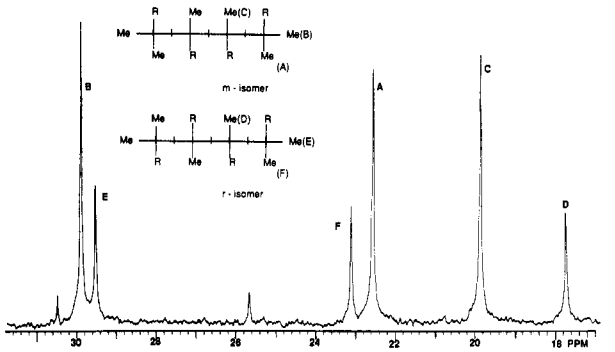


Figure 4. ^{13}C 50-MHz NMR spectrum of tetramer **3** (meso/racemic = 3/1) in TCE-d_2 at 25 °C. Absorptions at 25.7 and 30.5 ppm are unidentified.

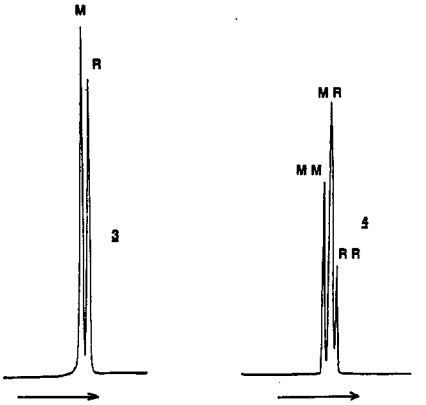


Figure 5. Gas chromatograms of LC fractions of tetramer **3** and pentamer **4**.

^1H and ^{13}C spectrum (Figure 4). For the ^{13}C NMR spectrum, the pro-m and pro-r terminal methyls are resolved for both stereoisomers, whereas in the ^1H spectrum, the downfield pro-r methyl absorptions flanked by a meso and racemic diad (H and M, respectively) are not resolved. As expected, the difference in chemical shift due to the difference in diad stereochemistry is less than that between the diastereotopic methyl end groups. In the latter case, the chemical shift difference is due to the adjacent asymmetric center, whereas the difference due to diad stereochemistry has its origin in the penultimate asymmetric center. The interior methyl groups for the m and r tetramers are clearly resolved in both spectra, the meso methyls absorbing downfield from the racemic methyls, as is also observed for the polymer. From integration of the methylene and methyl protons, the ratio of meso to racemic tetramer is about 3. This is confirmed by GC, the minor (r) isomer having the longest retention time (see Figure 5).

The stereochemistry of the pentamer 4 (sample A) is dominated by the mr and rr stereoisomers consistent with a predominant formation of r diads. Liquid chromatography provided a fraction with a high mr content (mr/rr = 5) as determined by GC (Figure 5). The proton spectrum is quite similar to that of the tetramer, with most of the terminal, internal, and central methyls being resolved. The methylene group of the meso diad in the rm isomer clearly shows the presence of an AB quartet as observed for the meso tetramer. Figure 6 shows the ^{13}C NMR spectrum of the mr/rr mixture. The two absorptions A_1 and A_2 corresponding to end methyls due to an adjacent meso diad (rm) and the four corresponding methyl absorptions (B_1, B_2, C_1, C_2) due to an adjacent r diad are clearly visible and were assigned on the basis of the ^{13}C NMR of the tetramer and from the known distribution of the pentamer stereoisomers. As is also observed in the

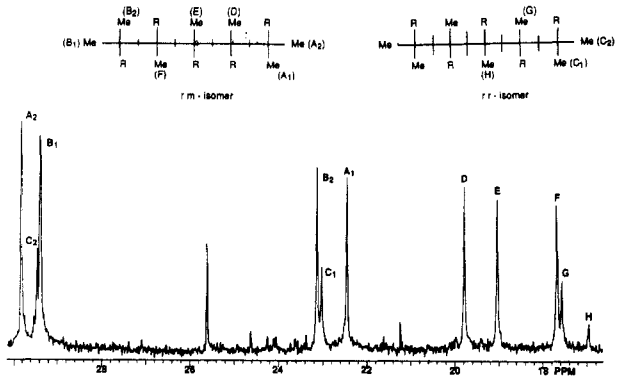


Figure 6. ^{13}C 50-MHz NMR spectrum of pentamer (mr/rr = 5/1) in TCE-d_2 at 25 °C. Unlabeled absorptions are unidentified.

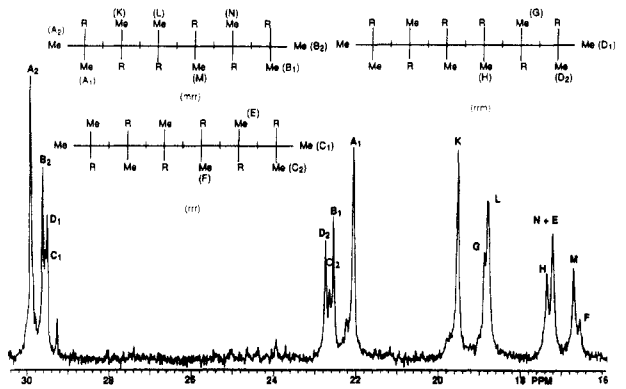


Figure 7. ^{13}C NMR (50-MHz) spectrum of hexamer 5 (mrr/rmr/rrr = 8/3/1) in TCE-d_2 at 25 °C. Unlabeled peaks are unidentified side products.

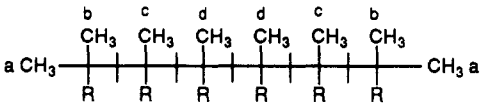
polymer, the central methyl (H) due to the rr sequence is upfield from that of the mr sequence (E) consistent with the stronger magnetic shielding of the methyl expected for the all-trans conformation of the rr triad. Consistent with this, the internal methyl (G) of the rr isomer likewise absorbs upfield from the internal methyl (F) of the rm isomer.

Hexamer stereochemistry was analyzed by isolation of two fractions by liquid chromatography followed by GC and NMR analysis. These fractions contained the rrm, rmr, and rrr stereoisomers in the ratios of 1/2/8 and 8/3/1, respectively. The ^{13}C NMR spectrum of the 8/3/1 fraction is shown in Figure 7. The assignments for the methyl groups are based upon that of the pentamer as well as on the composition of the two fractions and are collected in Table I together with the assignments for the other oligomers. The two groups of diastereotopic methyls are absorbing in the chemical shift ranges of 29.4–30.0 and 22.1–22.8 ppm, respectively. In the downfield region, the chemical shifts in order of increasing field are rrm* (A_2) < mrr* (B_2) < rrr* (C_1) < rmr* (D_1), and in the upfield region, this sequence is reversed.[10] The sensitivity of the terminal methyl groups to the stereochemistry of four preceding asymmetric centers is remarkable, and the above assignments are the basis for the corresponding end-group assignments in PMMA.[6,11] The central methyls are also of interest and absorb in the sequence *mrr* < *rmr* < m*rr* < *rrr* in order[11] of increasing field, consistent with the reported methyl shifts of PMMA.[12]

Stereochemistry of Oligomerization. Table II shows the stereochemistry of oligomerization of MMA carried out by initiation using lithioisobutyrate in THF at −78 °C (A) or the Na salt in toluene/THF (2/1 v/v) at −20 °C (B). The tetramer and pentamer prepared in THF in the presence of Li^+ have a high racemic diad content (0.92 and 0.93, respectively), and that of the hexamer appears to be even higher. These findings are in good accord with the substantial syndiotactic content of PMMA formed in THF at −78 °C in the presence of Li ion ($P_r > 0.88$). On the other hand, the oligomerization in the lower polarity medium (sample B) in the presence of Na ion leads to largely heterotactic oligomers.

Since the distribution of stereoisomers of oligomers 3–5 (sample B, Table II) reflects the actual distribution of the anion stereoisomeric precursors, the stereochemistry of formation of each oligomer could be evaluated by assuming that these precursors are equally reactive toward monomers. However, this leads to inconsistent results. For instance, although 4 mm of sample B comprises about one-fourth of the pentamer anions, the corresponding mmm$^-$ and mmr$^-$ anions are not present among the hexamer anions. Thus, either these hexamer anions are much more reactive toward monomers, leading to their depletion in the hexamer anion mixture, or they react preferentially through side reactions such as Claisen condensations.[8] Since such reactions were found to be prominent under the conditions of preparation of sample B, we think that the latter explanation is plausible. This conclusion is also supported by the demonstrated preferential depletion of the mm$^-$ polymer anion resulting from side reactions in this case.[11] Side reactions in the case of sample A do not seem to occur to a significant degree since the oligomerization temperature was much lower in this case (−78 °C). However, discrepancies due to different reactivities of stereoisomer anions have been documented in the oligomerization of 2-vinylpyridine[1] and its occurrence here would not be out of the question. Such results are obtained for the oligomerization at −78 °C in toluene initiated by the Li salts of ethyl and methyl isobutyrate (Table III). In

Table I
50-MHz ^{13}C NMR End Group and Main-Chain Methyl Carbon Chemical Shifts (in ppm from HMDS) for Methyl Methacrylate Oligomers in Tetrachloroethane-d_2 at 30 °C



	a	b	c	d
1	26.12	26.12		
2	29.48 (E)	22.99 (F)	18.35 (G)	
3 m	29I81 (B)	22.56 (A)	19.86 (C)	
3 r	29.56 (E)	23.10 (F)	I7.75 (D)	
4 *rm*	29.81 (A_2)	22.45 (A_1)	19.75 (D)	19.00 (E)
4 m*r*	29.46 (B_1)	23.10 (B_2)	17.67 (F)	19.00 (E)
4 rr	29.39 (C_2)	23.00 (C_1)	17.53 (G)	16.88 (H)
5 rr*m*	29.94 (A_2)	22.10 (A_1)	19.52 (K)	18.81 (L)
5 m*rr*	29.68 (B_2)	22.56 (B_1)	17.25 (N)	16.70 (M)
5 rrr	29.59 (C_1)	22.62 (C_2)	17.25 (E)	16.58 (F)
5 rmr	29.57 (D_1)	22.77 (D_2)	17.49 (H)	18.92 (G)

Table II
Stereochemistry Formation of Oligomers 3–5 As Determined by Gas Chromatography

oligomers	Li^+/THF, −78 °C (A)	Na/toluene:THF (2:1) −20 °C (B)
3 m	0.08	0.55
r	0.92	0.45
mm		0.26
4 mr	0.13	0.59
rr	0.87	0.15
mmm		
mmr		
5 mrm		0.19
rmr	0.03	0.47
mrr	0.06	0.31
rrr	0.91	0.04

Table III
Stereochemistry of Formation of Oligomers 8 and 9 at −78 °C As Determined by Gas Chromatography

		Li/toluene/EIB[a] (C)	Li/toluene/MIB[b] (D)	Li/THF/MIB (E)[b]
8	m[d]	0.36	0.24	c
	r[d]	0.64	0.76	
	mm[d]	0.12		
9	mr[d]	0.64	0.73	0.09
	rr[d]	0.24	0.27	0.91

[a] Derived from ethyl isobutyrate. [b] Derived from methyl isobutyrate. [c] Only trace amounts of protonated trimer were formed regardless of the monomer to initiator ratio. [d] Formation of m and r diads resulting from the protonation of the pro-meso and pro-racemic face of enolate, respectively. Thus 8 m corresponds to the 2*R*,4*S*/2*S*,4*R* isomer and 8 r to the 2*R*,4*R*/2*S*,4*S* isomer.

toluene, the methylation is extremely slow so that, in this case, the oligomerization was terminated by protonation (CH_3OH). The protonation of the trimer anion is not highly stereoselective, leading predominantly to 2*R*,4*S*/2*S*,4*R* isomer ("racemic" 8) in both cases. This has also been observed by Hatada and co-workers in their studies on the oligomerization of MMA by Grignard initiators.[3a] The distribution of anion stereoisomers is probably not affected by differences in their reactivity in side reactions at this low temperature. Assuming that the stereochemistry of protonation of the trimer and tetramer anion is identical, the proportions of m⁻ and r⁻ tetramer anion precursors may be calculated as 0.65/0.35 and 0.63/0.37 for the MMA addition to trimer initiated by MIB and EIB, respectively (Table III).

The results in THF (sample A) suggest that the protonation in this case occurs with predominant formation of "racemic" isomers.

Experimental Section

Oligomerization. The anionic oligomerization of methyl methacrylate was carried out under high vacuum (10^{-6} mmHg) by using break-seal techniques to add reagents. Methyl methacrylate was purified by distillation (2×). The last distillation was carried out from a CaH_2 slurry of MMA on the vacuum line. *N*-Lithiodiisopropylamide[13] was prepared by typically reacting 0.030 mol of diisopropylamine with 0.025 mol of *n*-butyllithium in hexane at 25 °C for 15 min. The hexane solution was then cooled to −78 °C a 5% molar excess of methyl isobutyrate was added, and the mixture was stirred for 30 min. The temperature was allowed to slowly rise to 0 °C, at which point the hexane and unreacted diisopropylamine and methyl isobutyrate were pumped off to leave a white powder. The lithiomethyl isobutyrate was dissolved in 250 mL of THF or toluene at −78 °C, and methyl methacrylate was added slowly by distillation into the initiator solution over a period of 2 h. The oligomerization was terminated by either methylation (methyl iodide) or protonation (methanol), or the solution was divided into two portions that were terminated differently. Termination was accomplished by adding a 5-fold excess of the terminating reagent to the oligomer solution and keeping the solution at −78 °C for 5 h. The terminated oligomer solution was then warmed to room temperature, and the solvent was removed in vacuo. The oligomers were redissolved in chloroform and washed three times each with saturated NH_4Cl followed by saturated aqueous $NaHCO_3$ and finally water. The chloroform solution was dried over 5-Å molecular sieves and evaporated.

Sample B was kindly made available to us by Dr. L. Lochmann. This sample was prepared in a similar manner by using sodiobis(trimethylsilyl)amide to deprotonate the isobutyrate ester.

Isolation of the oligomers was carried out with an Altex Model 332 gradient liquid chromatograph equipped with a Merck Lobar B column, packed with 40–63-μm Li Chroprep Si-60 silica gel. The eluent was a 1/8 (v/v) acetonitrile/*n*-butyl chloride mixture at a flow rate of 4.2 mL/min.

Characterization. Gas chromatographic analysis of the oligomer mixture was done on a Hewlett-Packard Model 5880A instrument equipped with a capillary column in a temperature-programmable oven. The column was a 50-m fused silica capillary (0.3 mm i.d.) coated with a 0.17-μm film of silicone gum. A multilevel temperature program was used to increase speed and resolution. The temperature program was designed such that the oligomers eluted at constant temperature.

NMR spectra were obtained in 1,1,2,2-tetrachloroethane-d_2 solutions at 30 °C on a Varian XL-200 spectrometer operating at 200 MHz (^{13}C NMR). The ^{13}C NMR spectra (2500–8000 transients) were acquired by using a 5.5-s pulse delay. Before Fourier transformation, the FID were multiplied by an increasing exponential function to enhance resolution.

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Registry No. PMMA, 9011-14-7; THF, 109-99-9; CH_3OH, 67-56-1; CH_3I, 74-88-4; $(CH_3)_2CHCO_2CH_2^-\cdot Na^+$, 128661-27-8; $(CH_3)_2CHCO_2CH_2^-\cdot Li^+$, 128661-28-9; toluene, 108-88-3.