

This article was downloaded by:

On: 24 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>

Synthesis of N-Acryl-N,N'-di-tert-Butylurea and Copolymerization with Ethylene Glycol Dimethacrylate

Ana Erceg Kuzmić^a; Štefica Podolski^a; Grozdana Bogdanić^a; Radivoje Vuković^a

^a INA-Industrija nafte, d.d., Research and Development Sector, Lovinčičeva b.b., Zagreb, Croatia

To cite this Article Kuzmić, Ana Erceg, Podolski, Štefica, Bogdanić, Grozdana and Vuković, Radivoje(2006) 'Synthesis of N-Acryl-N,N'-di-tert-Butylurea and Copolymerization with Ethylene Glycol Dimethacrylate', Journal of Macromolecular Science, Part A, 43: 6, 879 – 887

To link to this Article: DOI: 10.1080/10601320600653673

URL: <http://dx.doi.org/10.1080/10601320600653673>

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.

Synthesis of N-Acryl-N,N'-di-tert-Butylurea and Copolymerization with Ethylene Glycol Dimethacrylate

ANA ERCEG KUZMIĆ, ŠTEFICA PODOLSKI,
GROZDANA BOGDANIĆ, AND RADIVOJE VUKOVIĆ

INA-Industrija nafte, d.d., Research and Development Sector, Lovinčićeva b.b.,
Zagreb, Croatia

Synthesis and free-radical initiated copolymerization of N-acryl-N,N'-di-tert-butylurea (A-DitBuU) with ethylene glycol dimethacrylate (EDMA) are described. The A-DitBuU monomer was prepared by the condensation of acrylic acid to the N,N'-di-tert-butylcarbodiimide (DitBuC) at room temperature. Copolymers of A-DitBuU with EDMA of different monomer to monomer ratios in the feed were prepared in the presence of dibenzoyl peroxide (Bz₂O₂) in butanone at 70°C for 48 h up to a high conversion. The obtained crosslinked copolymers are insoluble in organic solvents. Copolymers thermal decomposition resulted in separation of tert-butylnisocyanate (C₄H₉NCO) in the temperature range between 180 and 280°C and by the formation of the thermally stable molecularly imprinted copolymers of N-acryl-N-tert-butylamide (A-tBuA) with EDMA.

Keywords N-acryl-N,N'-di-tert-butylurea, poly(N-acryl-N,N'-di-tert-butylurea-co-ethylene glycol dimethacrylate), thermal degradation, tert-butylnisocyanate, poly(N-acryl-N-tert-butylamide-co-ethylene glycol dimethacrylate)

Introduction

Recently, a molecular imprinting has emerged as a powerful technique which provides predetermined selectivity for various substances in synthetic polymers. Many factors determine the structure, recognition properties of crosslinked imprinted polymers, e.g., the monomer composition, relative monomer reactivity, level of crosslinking, the nature and volume of solvent, temperature, initiator and initiator concentration and method of initiation, will all influence to some extent the structure of the polymers (1–5). Two essentially different approaches have been developed, covalent (1) and non-covalent (3) molecular imprinting. In both cases, the functional monomers, chosen so as to allow interactions with the functional groups of the imprint molecule, are polymerized in the presence of the imprint molecule. Once polymerization is over, the print molecules are removed and the resulting polymer contains recognition sites which are complementary

Received and Accepted December 2005.

Address correspondence to Radivoje Vuković, INA-Industrija nafte, d.d., Research and Development Sector, Lovinčićeva b.b., POB 555, 10002 Zagreb, Croatia. Fax: +385 1 245 2794; E-mail: radivoje.vukovic@ina.hr

in shape to the template (6). Molecular imprinting of the desired molecules into selected crosslinked polymers is of interest for practical application in different fields (7): in analytical chemistry (8), synthetic chemistry (9), the food industry (10), biotechnology (11), and materials chemistry (12, 13).

One problem in molecular imprinting concerns the small amount of template that remains bound to the polymer after an attempted extraction. This may constitute a problem when materials are used in analytical quantification of low levels of analytes. In the recently published paper, Ellwanger et al. (14) evaluated the methods aimed at complete removal of the template from molecularly imprinted polymers. This problem is overcome in the molecular imprinting procedure in our laboratories, based on the selective thermal decomposition of crosslinked copolymers of (meth)acryl-dicyclohexylurea [(MA)A-DCU] (15–18) and methacryl-diisopropylurea (MA-DiPrU) (19) with bifunctional monomer, ethylene glycol dimethacrylate (EDMA). In the preparation of crosslinked copolymers of acryl-DCU, methacryl-DCU and methacryl-DiPrU with EDMA high differences in the polymer yield were obtained. Namely, by the polymerization of acryl-DCU with EDMA conversion of 99%, regardless of the ratio of comonomers in the feed, in the presence of 1% of Bz_2O_2 during 20 hrs, at 70°C, was obtained (15). For both methacrylic systems (copolymers of MA-DCU with EDMA and MA-DiPrU with EDMA), it was found that the conversion depended on the comonomer molar ratio in the feed and changes from 84 to 30 wt% by changing MA-DCU or MA-DiPrU in the feed from 0.3 to 0.8 (2% of Bz_2O_2 , 48 h, 70°C) (17, 19).

Thermal behavior for all prepared copolymers was similar. All decomposed under TGA conditions (in nitrogen, heating rate 10°C/min, temperature range 180–450°C) by a two-step mechanism. In the first step at temperature between 180–250°C, separation of cyclohexylisocyanate or isopropylisocyanate occurred. The residue identified as a crosslinked copolymer of (meth)acryl-cyclohexylamide [(meth)acryl-CHA] or methacryl-isopropylamide (methacryl-iPrA) with EDMA was thermally stable up to 280°C. These copolymers contained a molecularly imprinted structure.

In the present paper, we wish to describe the synthesis and copolymerization of acryl-di-tert-butylurea (A-DitBuU) with EDMA, thermal stability and mechanism of copolymers thermal degradation in the continuation of this work. A comparison between the condensation process of A-DitBuU monomer preparation and acryl-DCU, as well as the influence of the tert-butyl group bulkiness to the polymerization was presented. Molecularly imprinted copolymer content, obtained by the thermal degradation of A-DitBuU with EDMA copolymers of different copolymer composition, will also be discussed.

Experimental

Synthesis of N-Acryl-N, N'-di-tert-Butylurea

To the solution of 2.315 g (0.015 mol) of DitBuC (Sigma-Aldrich Chemie GmbH, Steinheim, Germany, 99%) in 3 mL of tetrahydrofurane (THF) (Fluka, Buchs, Switzerland), under stirring at room temperature, the solution of 1.08 g (0.015 mol) of acrylic acid (AA) (Fluka, Buchs, Switzerland, ≥99%) in 3 mL of THF, was gradually added. After standing overnight at room temperature the clear reaction mixture was evaporated in vacuum without heating to dryness, treated with 40 mL of diethyl ether (Kemika, Zagreb, Croatia, p.a.), left overnight in a refrigerator. Afterward, the white crystalline product was filtered off yielding 1.813 g (53.4%) of an analytically pure A-DitBuU monomer; melting at 130–132°C.

Analysis: Calcd. for $C_{12}H_{22}N_2O_2$ (226) (%): C, 63.72; H, 9.73; N, 12.39. Found: C, 63.32; H, 9.57; N, 12.27.

The structure of the A-DitBuU was proved by IR and NMR spectra. It noteworthy interest that the synthesis of A-DitBuU proceeded without any conversion of carboxylic acid to acrylic anhydride, which was not the case in the previously described preparation of N-(meth)acryl-DCU (20) and N-methacryl-DiPrU monomers (19). Another difference with respect to the monomer preparation was observed. Namely, A-DitBuU monomer was isolated without the addition of a polymerization inhibitor, which was not the case in the preparation of N-acryl-DCU. This behavior indicated that the condensation process in A-DitBuU synthesis was highly influenced by the tert-butyl group bulkiness. Due to the same reason, it was expected that the polymerization process would be hindered.

Polymerization Procedure

Homopolymerization of A-DitBuU and copolymerization with EDMA (Aldrich, Steinheim, Switzerland, 98%) was carried out in glass reaction tubes (10 mL), thoroughly degassed, filled with nitrogen before sealing, and placed into the oil bath thermostated at 70°C. Polymerization was initiated with 2 wt% of Bz_2O_2 (Fluka, Buchs, Switzerland, 97%) in butanone (Fluka, Buchs, Switzerland, purum). After polymerization, the solution was cooled to room temperature and washed with butanone in order to remove the unreacted monomers, dried in vacuum overnight at 80°C, and used for further analysis.

Homopolymerization of A-DitBuU

The procedure applied for the homopolymerization of A-DitBuU was as follows: 0.452 g of A-DitBuU dissolved in 1 mL butanone containing 2 wt% (0.00904 g) of Bz_2O_2 was polymerized in N_2 at 70°C for 48 h. During that period, no change in the sample was observed. After cooling to room temperature, the solution was added to methanol. No precipitated product was observed. In repeating the experiment, polymerization was performed under the same conditions during 120 h. The result was the same. Therefore, it was concluded that A-DitBuU did not polymerize.

Copolymerization of A-DitBuU with EDMA at Molar Ratio of 0.5 to 0.5 in the Feed

1 mL of butanone containing 2 wt% (0.0085 g) of Bz_2O_2 as initiator was added to the mixture of 0.226 g (0.001 mol) of A-DitBuU and 0.198 g (0.001 mol) of EDMA. After heating for 48 h at 70°C in nitrogen, the copolymer was cooled at room temperature and washed with butanone, yielding 0.369 g (86.97%) of insoluble copolymer. Under the same experimental conditions, the crosslinked copolymers of A-DitBuU with EDMA at monomer to monomer ratios of 0.2/0.8; 0.3/0.7; 0.7/0.3; 0.8/0.2 in the feed were also prepared. The comonomer molar ratios, polymerization conditions and elemental analysis data of the copolymers are presented in Table 1.

Measurements

Elemental analysis data were obtained by a LECO CHNS-932 automatic analysis. The NMR spectra were recorded on a Bruker Avance 300 FT NMR spectrometer. The IR

Table 1
Polymerization conditions and properties of copolymers of
A-DitBuU with EDMA

| Molar fraction of A-DitBuU | | Yield (g) | Conversion (%) | Elemental analysis | T _g (°C) |
|-------------------------------|-----------------|--------------|-------------------|--------------------------------|------------------------|
| In feed | In copolymer | | | | |
| 0.20 | 0.18 | 0.396 | 97.27 | C, 58.20 H, 7.52 N, 2.18 | 172 |
| 0.30 | 0.27 | 0.387 | 93.75 | C, 58.67 H, 7.81 N, 3.34 | 179 |
| 0.50 | 0.45 | 0.369 | 86.98 | C, 58.43 H, 8.24 N, 5.60 | 188 |
| 0.70 | 0.62 | 0.367 | 84.42 | C, 59.22 H, 8.62 N, 7.68 | 198 |
| 0.80 | 0.72 | 0.362 | 82.10 | C, 60.49 H, 8.92 N, 8.93 | 208 |

Total monomer concentration 2M/L; butanone; 2 wt% Bz₂O₂; 70°C; 48 h; nitrogen.

Perkin-Elmer Spectrum One spectrometer was used in monomer analysis. Differential scanning calorimetry was carried out on the Perkin-Elmer Diamond DSC with a scanning rate of 40°C/min in nitrogen and the sample size of about 15 mg. Glass transition temperature, T_g, was taken as the inflection point of the heat capacity discontinuation in the first scan. Thermogravimetric measurements were made with the Perkin-Elmer Pyris 6 TGA at a heating rate of 10°C/min, in nitrogen.

Results and Discussion

Thermal behavior of the crosslinked copolymers of A-DitBuU with EDMA of a different copolymer composition was investigated by using TGA in nitrogen atmosphere in the temperature range between 100 and 450°C. The thermograms are presented in Figure 1. It is evident that, regardless of the ratio of comonomers in copolymers, they decompose by a two-step mechanism. The first step started at almost 180°C and resulted in tert-butylisocyanate (C₄H₉NCO) separation (as proved by IR, NMR and elemental analysis data) in the quantity dependent on the copolymer composition. The C₄H₉NCO yield increased by the increasing A-DitBuU concentration in the copolymers (Table 2).

The amount of the volatile fraction closely corresponds to the theoretical value of C₄H₉NCO removal, as shown in Table 2. The resulting residues are crosslinked

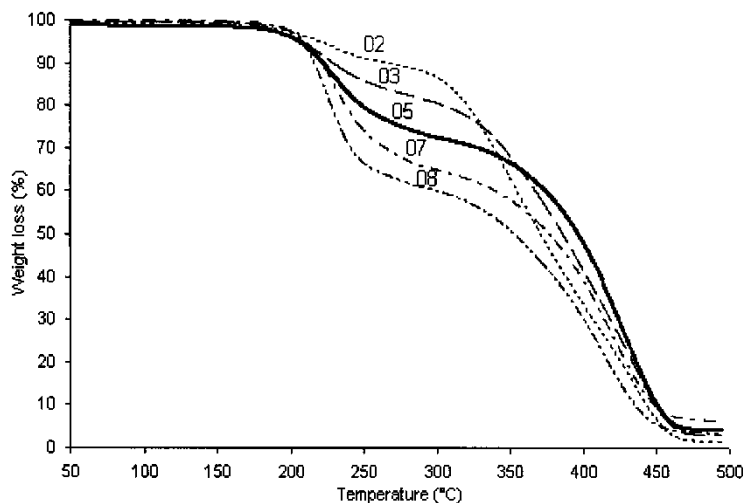


Figure 1. Thermograms of the crosslinked copolymers of A-DitBuU with EDMA at molar ratios of comonomers in the feed: 0.2/0.8; 0.3/0.7; 0.5/0.5; 0.7/0.3; 0.8/0.2.

imprinted copolymers of N-acryl-N-tert-butylamide (A-tBuA) with EDMA. Thermal stability of these copolymers is not significantly different as can be seen from Figure 2. The results show a high thermal stability of these copolymers up to 280°C. Afterwards, the copolymers decompose in one step up to 450°C.

A comparison between the crosslinked copolymers of poly(A-DitBuU-co-EDMA) and poly(A-DCU-co-EDMA), as well as between the theoretical and measured values of volatile fraction in copolymers was also made (Table 3 and Figure 3).

In both copolymers, the amount of volatile product, i.e., C_4H_9NCO or $C_6H_{11}NCO$, based on TGA thermograms, corresponds to the values based on loss of nitrogen by thermal degradation of poly(A-DitBuU-co-EDMA) and poly(A-DCU-co-EDMA) copolymers. It is also evident that a higher imprinted polymers yield was obtained by thermal degradation of poly(A-DCU-co-EDMA) copolymers.

Molecularly imprinted crosslinked copolymers of acryl-cyclohexylamide (A-CHA) showed a higher thermal stability and did not degrade until 400°C (Figure 3). It may be attributed to an improvement of these copolymers integrity.

Thermal behavior of copolymers of A-DitBuU with EDMA showed that the mechanism of preparation of molecularly imprinted crosslinked copolymers corresponded to the previously described for the thermal degradation of poly(MA-DiPrU-co-EDMA) (19) or poly(MA-DCU-co-EDMA) (17). The possible mechanism of the thermal degradation of crosslinked copolymers of A-DitBuU with EDMA, based on the identified volatile product, C_4H_9NCO , is illustrated in Scheme 1.

According to Scheme 1, by applying the numbering of atoms in the repeating units of A-DitBuU, as proposed by Newman in Rule of Six (21), hydrogen atom 6 in the coiled structure of di-tert-butylurea linked to the carboxyl group of the acrylic acid 1, 2 comes close to the $-C-N-$ atoms 2 and 3. At a temperature of about 180°C, hydrogen 6 reacts with tert-butylamine 3, thus causing the separation of C_4H_9NCO (Scheme 1b). As a result of the tert-butylisocyanate separation, the crosslinked poly(A-tBuA-co-EDMA) containing the recognition groups $-CO-NH-$ (Scheme 1c) was formed.

Table 2
Composition of copolymers of A-DitBuU with EDMA, theoretical and measured values of C₄H₉NCO in copolymers

| Molar fraction of A-DitBuU | | C ₄ H ₉ NCO (%) | | | | |
|----------------------------|---|--|--|--|---|---------------------------------------|
| In feed | In copolymer (based on N ₂) | A-DitBuU-co-EDMA ^a (N ₂ content in copolymer, %) | A-tBuA-co-EDMA ^b (N ₂ content in copolymer, %) | Molar fraction of A-tBuA in copolymer (based on N ₂) | Based on thermal degradation (loss of N ₂) ^c | Based on TGA thermograms ^d |
| 0.20 | 0.18 | 2.18 | 1.37 | 0.12 | 11.7 | 11.0 |
| 0.30 | 0.27 | 3.34 | 1.97 | 0.18 | 19.8 | 18.5 |
| 0.50 | 0.45 | 5.60 | 4.10 | 0.37 | 21.8 | 21.3 |
| 0.70 | 0.62 | 7.68 | 6.11 | 0.55 | 24.2 | 26.2 |
| 0.80 | 0.72 | 8.93 | 7.06 | 0.64 | 29.2 | 33.8 |

^aPolymerization conditions; 70°C, 2% Bz₂O₂; total monomer concentration 2 M/L; butanone; 48 h.

^bPolymers obtained by thermal degradation of copolymers (a) in TGA for 5 min at 250°C, in nitrogen.

^cBased on the loss of nitrogen during the preparation of copolymers (b) by thermal degradation of copolymers (a).

^dFrom the weight loss in thermograms at 250°C.

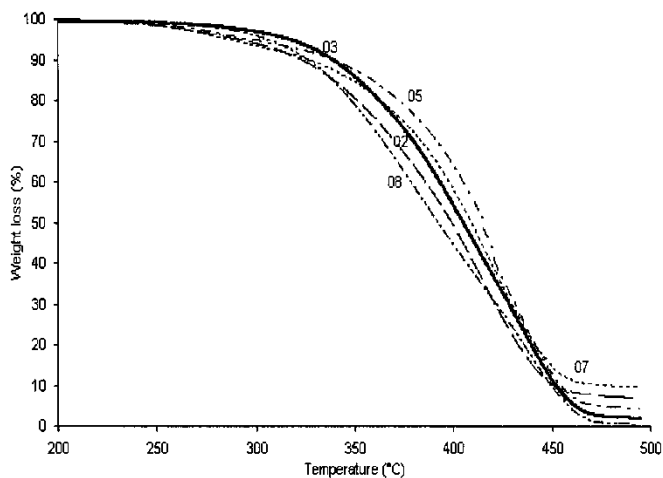


Figure 2. Thermograms of the imprinted copolymers of A-tBuA with EDMA obtained after removal of C_4H_9NCO from the copolymers of A-DitBuU with EDMA at molar ratios of: 0.2/0.8; 0.3/0.7; 0.5/0.5; 0.7/0.3; 0.8/0.2.

Conclusions

A-DitBuU monomer was prepared by direct condensation of DitBuC and AA at room temperature. Contrary to the previously published preparation of the corresponding acrylic monomer containing DCU as a pendant group, in which a portion of DCU separated, the indication is that a portion of acrylic acid was converted to acid anhydride. It is noteworthy that A-DitBuU was isolated without the addition of a polymerization inhibitor, which was not the case in the preparation of A-DCU.

Table 3

Comonomer and copolymer composition of copolymers of A-DitBuU and A-DCU with EDMA, theoretical and measured values of volatile fraction in copolymers

| Molar fraction of A-DitBuU ¹ or A-DCU ² In feed | In copolymer (based on N ₂) | N ₂ content in copolymer (%) | Volatile fraction C ₄ H ₉ NCO ¹ or C ₆ H ₁₁ NCO ² (%) | |
|---|--|--|--|-----------------------------|
| | | | Based on thermal degradation (loss of N ₂) | Based on TGA thermograms |
| 0.30 ¹ | 0.27 | 3.34 | 19.8 | 18.5 |
| 0.30 ² | 0.36 | 3.58 | 15.0 | 17.0 |
| 0.50 ¹ | 0.45 | 5.60 | 21.8 | 21.3 |
| 0.50 ² | 0.57 | 5.74 | 21.0 | 26.3 |
| 0.70 ¹ | 0.62 | 7.68 | 24.2 | 26.2 |
| 0.70 ² | 0.75 | 7.55 | 30.5 | 34.4 |
| 0.80 ¹ | 0.72 | 8.93 | 29.2 | 33.8 |
| 0.80 ² | 0.82 | 8.25 | 35.4 | 38.1 |

The crude crosslinked residue after the removal of C_4H_9NCO , copolymer of A-tBuA with EDMA (imprinted copolymer), decomposed by a one-step mechanism in the temperature range of 280 to 450°C.

A comparison of the A-DitBuU with EDMA and A-DCU with EDMA copolymers was made. There were no significant differences found in the thermal behavior of those systems.

Acknowledgement

The Ministry of Science, Education and Sport of the Republic of Croatia supported this work.

References

1. Wulff, G. (1995) *Angew. Chem. Int. Ed. Engl.*, 34: 1812–1832.
2. Shea, J.K. (1994) *Trends Polym. Sci.*, 2 (5): 166–173.
3. Mosbach, K. (1994) *Trends Biochem. Sci.*, 19: 9–14.
4. Sellergren, B. (2000) *Angew. Chem. Int. Ed. Engl.*, 39 (6): 1031–1037.
5. Haupt, K. (2003) *Anal. Chem.*, 75: 377A–383A.
6. Wulff, G. (1993) *Trends Biochem. Sci.*, 11: 85–87.
7. Whitcombe, J.M. and Vulfson, N.E. (2001) *Adv. Mater.*, 13 (7): 467–477.
8. Andersson, I.L. (2000) *J. Chromatogr. B.*, 745: 3–13.
9. Whitcombe, J.M., Alexander, C., and Vulfson, N.E. (2000) *Synlett.*, 6: 911–923.
10. Whitcombe, J.M., Alexander, C., and Vulfson, N.E. (1997) *Trends Food Sci. Technol.*, 8: 140–145.
11. Andersson, I.L. (2000) *J. Chromatogr. B.*, 739: 163–173.
12. Haupt, K. and Mosbach, K. (2000) *Chem. Rev.*, 100: 2495–2504.
13. Kempe, M. and Mosbach, K. (1995) *J. Chromatogr. A.*, 694: 3–13.
14. Ellwanger, A., Berggren, C., Bayouhd, S., Crecenzi, C., Karlson, L., Owens, K., Paul, K., Ensing, K., Cormack, P., Sherrington, D., and Sellergren, B. (2001) *Analyst*, 126: 784–792.
15. Erceg Kuzmić, A., Vuković, R., Bogdanić, G., and Fleš, D. (2003) *J. Macromol. Sci.-Pure Appl. Chem.*, A40 (1): 81–85.
16. Erceg Kuzmić, A., Vuković, R., Bogdanić, G., and Fleš, D. (2003) *J. Macromol. Sci.-Pure Appl. Chem.*, A40 (8): 747–754.
17. Erceg Kuzmić, A., Vuković, R., Bogdanić, G., and Fleš, D. (2004) *J. Macromol. Sci.-Pure Appl. Chem.*, A41 (8): 907–912.
18. Šmit, I., Erceg Kuzmić, A., Vuković, R., Bogdanić, G., and Fleš, D. (2005) *J. Macromol. Sci.-Pure Appl. Chem.*, A42 (12): 1621–1626.
19. Erceg Kuzmić, A., Vuković, R., Bogdanić, G., Špehar, B., and Fleš, D. (2004) *J. Macromol. Sci.-Pure Appl. Chem.*, A41 (10): 1087–1094.
20. Erceg, A., Vuković, R., Bogdanić, G., Piližota, V., and Fleš, D. (2000) *J. Macromol. Sci.-Pure Appl. Chem.*, A37 (11): 1363–1375.
21. Newman, S.M. (1950) *J. Am. Chem. Soc.*, 72: 4783–4785.