[Downloaded free from http://www.jpbsonline.org on Sunday, June 6, 2021, IP: 106.197.71.153]

Original Article

Synthesis and Characterization of a Ring-Opening Oxaspiro Comonomer by a Novel Catalytic Method for Denture Base Resins

Ranganathan Ajay, Vikraman Rakshagan[1], Rajamani Ganeshkumar[2], Elumalai Ambedkar[2], Shafiullah RahmathShameem[2], Kanagesan Praveena[3]

Department of Prosthodontics and Crown and Bridge, Vivekanandha Dental College for Women, Namakkal, [1]Department of Prosthodontics and Implant Dentistry, Saveetha Dental College and Hospital, Saveetha Institute of Medical and Technical Science, Saveetha University, [2]Department of Prosthodontics and Crown and Bridge, Sri Venkateswara Dental College and Hospital, Chennai, [3]Department of Prosthodontics and Crown and Bridge, JKK Nattraja Dental College and Hospital, Komarapalayam, Tamil Nadu, India

Submitted: 16-Sep-2020
Revised: 15-Oct-2020
Accepted: 24-Nov-2020
Published: 05-Jun-2021.

ABSTRACT

Background: 3,9-Dimethylene-1,5,7,11-tetraoxaspiro[5,5]undecane (DMTOSU) is a double ring-opening monomer that exhibits expansion upon polymerization and may be used as a denture base resin's comonomer to offset or minimize polymerization shrinkage. It's synthesis by transesterification reaction (TE) catalyzed by distannoxane is not reported in the literature. The synthesis became the prime concern because this monomer is hardly available commercially. **Purpose:** The purpose is to confirm the DMTOSU synthesis and compare the synthesized monomers obtained by two different catalytic processes through Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies. **Materials and Methods:** Scheme I synthesis was by TE catalyzed by dichlorotetrabutyl distannoxane (DCBS) yielding M1 monomer. Scheme II synthesis was catalyzed by dibutyltin oxide-carbon disulfide (DBTO-CS_2) yielding M2 monomer. **Results:** The appearance of a characteristic peak at 1212 cm^{-1} in FTIR spectrum, a doublet at δ 4.95 in ^{1}H-NMR spectrum and a peak at δ 117.12 in ^{13}C-NMR spectrum confirmed the synthesis of DMTOSU-M1catalyzed by DCBS, which is not significantly different from DMTOSU-M2 catalyzed by DBTO-CS_2. **Conclusion:** The catalytic action of DCBS is a successful alternative to the DBTO-CS_2 catalysis in DMTOSU synthesis.

KEYWORDS: *Catalyst, denture base resins, oxaspiro monomer, polymerization shrinkage, ring-opening*

INTRODUCTION

Poly(methyl methacrylate) (PMMA) used for the fabrication of denture bases (DB) suffers dimensional errors during processing and clinical use. The dimensional errors are directly attributed to the PMMA material used.[1] The processing shrinkage is one of the dimensional errors of PMMA, which is extensively documented in the dental literature.[1-6] Volumetric shrinkage of around 20%–21% was observed when methyl methacrylate monomer is directly polymerized to PMMA.[7-9] Volumetric shrinkage of 5%–9% is observed when the monomer is blended with the polymer.[8,10-12] The denture shrinkage along the posterior palatal region and lingual flanges antero-posteriorly compromises the retention and exerts pressure on the disto-buccal aspect of tuberosity, disto-lingual and antero-labial regions of the mandibular arch.[13-17] Pathological bone resorption[18,19] and vertical occlusal discrepancies[20] are the common sequel of polymerization shrinkage. Therefore, from the above context, shrinkage of the PMMA DB resins is an unresolved problem for many decades.

The polymerization method and processing technique were modified in an attempt to reduce the dimensional errors.[21,22] Furthermore, concerning the material, various additives such as synthetic fibers, metallic wires, inorganic fillers, and rubber toughening agents have been incorporated in the acrylic resin to reduce

Access this article online

Quick Response Code:

Website: www.jpbsonline.org

DOI: 10.4103/jpbs.JPBS_524_20

Address for correspondence: Dr. Ranganathan Ajay, Department of Prosthodontics and Crown and Bridge, Vivekanandha Dental College for Women, Elayampalayam, Tiruchengode, Namakkal - 637 205, Tamil Nadu, India.
E-mail: jrangclassiq@gmail.com

This is an open access journal, and articles are distributed under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike 4.0 License, which allows others to remix, tweak, and build upon the work non-commercially, as long as appropriate credit is given and the new creations are licensed under the identical terms.

For reprints contact: WKHLRPMedknow_reprints@wolterskluwer.com

How to cite this article: Ajay R, Rakshagan V, Ganeshkumar R, Ambedkar E, RahmathShameem S, Praveena K. Synthesis and characterization of a ring-opening oxaspiro comonomer by a novel catalytic method for denture base resins. J Pharm Bioall Sci 2021;13:S521-6.

[Downloaded free from http://www.jpbsonline.org on Sunday, June 6, 2021, IP: 106.197.71.153]

the shrinkage.[23-25] However, monomeric modifications are not uncommon.[26] A PMMA copolymer with hydrophobic Norbonyl-and phenyl-methacrylate comonomers exhibited less polymerization shrinkage.[9]

Nevertheless, the advent of ring-opening monomers (spiroorthoesters, bicycloorthoesters, and spiroorthocarbonates [SOC]) has a promising effect on the dimensional stability of a polymer by rendering it shrink-free by exhibiting volumetric expansion upon polymerization.[27] SOCs are the most widely researched and evaluated monomers owing to the most significant volume expansions. This is because of the compact nature of the bicyclic monomers and the open-chain structure upon polymerization that can be further cross-linked or copolymerized.[28] 3,9-Dimethylene-1,5,7,11-tetraoxaspiro[5,5] undecane (DMTOSU) is one such symmetrical oxaspiro double ring-opening SOC monomer with two exocyclic methylene group. However, the effects of adding SOC as comonomers in denture base resin on physico-mechanical properties and biocompatibility have not been reported yet in the dental literature.

A classic, time-consuming, two-step synthesis of DMTOSU is through di-*n*-butyl tin-oxide (DBTO) – carbon disulfide (CS_2) catalysis.[27] Transesterification reaction (TE) is also a method for synthesizing SOC monomers even under anhydrous conditions.[29] In the previous researches, TE synthetic reactions of SOCs were catalyzed by *p*-toluene sulfonic acid.[30,31] 1,3-dichloro-1,1,3,3-tetrabutyl distannoxane [Cl $(C_4H_9)_2$Sn–O–Sn $(C_4H_9)_2$Cl] $_2$ (DCBS) is a distannoxane (DS) Otera's catalyst and intelligible weak Lewis acid. It has a peculiar ladder structure rendering it structurally stable. DCBS exists as a dimer and due to its high lipophilicity and multi-active catalytic centers, it is superior to alkali or other transesterification catalysts.[32] However, the synthesis of DMTOSU by TE catalyzed by DCBS is not yet reported in the literature. Hence, the present study aims to confirm the DMTOSU synthesis by TE reaction catalyzed by DCBS and compare it with the DMTOSU synthesis catalyzed by dibutyltin oxide-carbon disulfide (DBTO-CS_2) through Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies. The null hypothesis is that the syntheses of DMTOSU by the two individual catalytic reactions would have no significant differences.

Materials and Methods

2-methylene-1,3-propanediol (MPD; $C_4H_8O_2$: 97%), tetraethyl orthocarbonate (TEOC; $C_9H_{20}O_4$: 97%), 1,3-dichloro-1,1,3,3-tetrabutyl distannoxane (DCBS; $C_{16}H_{36}Sn_2O$: 98%), di-n-butyl tinoxide (DBTO; $C_8H_{18}SnO$: 98%), and carbon disulfide (CS_2) were purchased from Aldrich Co., (Sigma-Aldrich, St. Louis, MO, USA) and used without further purification.

Scheme I – Synthesis of 3,9-Dimethylene-1,5,7, 11-tetraoxaspiro[5,5]undecane (M1) by TE catalyzed by DCBS

In a three-necked, 250 mL, round-bottom flask provided with magnetic stirrer, condenser, nitrogen inlet, and thermometer, were put in 2 g of molecular sieves and 60 mL of toluene. Then 56.74 mmol of MPD and 1.44 mmol of DCBS were also added. After 15 min were added 9.51 mmol of TEOC and 10.45 mmol of Na_2CO_3. The system was flushed with nitrogen to set anhydrous conditions, and the reaction was left for 3 h at 100°C. During the reaction, ethanol was promptly allowed to escape through a distillation column. Triethylamine (0.3 mL) was added to stop the reaction and the solution was left to cool to room temperature. After the reaction time, the reaction mixture was filtered and the solvent was rotoevaporated, obtaining M1 as white precipitate, which was then recrystallized from *n*-hexane or acetone [Figure 1: Scheme I].

Scheme II – Synthesis of 3,9-Dimethylene-1,5,7, 11-tetraoxaspiro[5,5]undecane (M2) catalyzed by dibutyltin oxide-carbon disulfide

The three-necked flask was charged with 51.29 mmol of MPD, 51.36 mmol of DBTO, and 80 mL of toluene. The mixture was gradually heated up to 85°C at which toluene-water azeotrope was collected. This azeotrope collection was performed for 6 h till the temperature reached to 111°C (boiling point of toluene). This left a clear solution of cyclic tin intermediate, which was allowed to cool under argon to room temperature. This was followed by the addition of 40.22 mmol of CS_2 in 30 mL of toluene. The mixture was stirred at 80°C for 5 h and toluene was stripped in vacuo. The formed product was isolated from the reaction by-product, dibutyltin sulfide ($SnBu_2S$), by

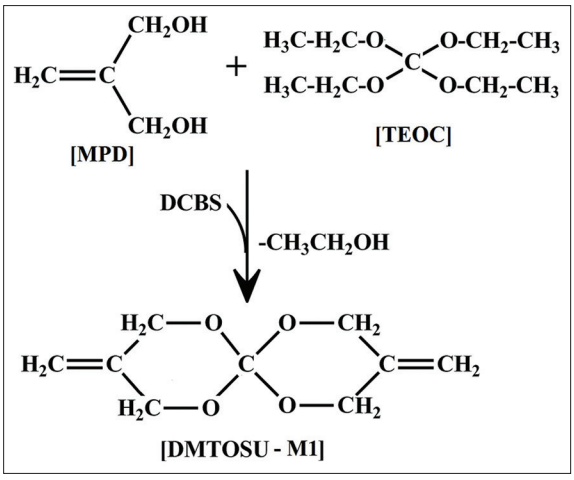


Figure 1: Scheme I – Synthesis of 3,9-Dimethylene-1,5,7,11-tetraoxaspiro[5,5]undecane (M1) by TE catalyzed by DCBS

[Downloaded free from http://www.jpbsonline.org on Sunday, June 6, 2021, IP: 106.197.71.153]

distillation contained at 2–5 mm pressure until the flask temperature reached 180°C. The distillate product M2 crystallized to wet solid with 92% yield as it was collected. The obtained product was then purified by sublimation after recrystallization from *n*-hexane [Figure 2: Scheme II].

To confirm and compare the synthesis of M1 and M2, the FTIR spectra were recorded by potassium bromide (KBr) pellet technique (ThermoScientific™ Nicolet™ iS™ 5; iD1 Transmission, Waltham, MA; USA) at a resolution of 4 cm^{-1} and 32 scans in the range of 4000–600 cm^{-1}. A digital NMR spectrometer (Ultrashield™ 400 Plus; Bruker BioSpin, Karlsruhe, Germany) was used for recording ^{1}H-and ^{13}C-NMR spectra. M1 and M2 were taken in a thin glass tube to which 1 mL of deuterated chloroform ($CDCl_3$) was added and shaken well for dissolution.

Results

Infrared spectra analysis displayed several peaks of M1 and M2 monomers. Table 1 describes the functional groups and spectral wave numbers of the monomers. Figure 3 shows the transmitted spectra of M1. The peak signals of ^{1}H- and ^{13}C-NMR of M1 are shown in Figures 4 and 5, respectively. The peak intensities of M1 and M2 monomers are tabulated in Table 2. The appearance of the characteristic peculiar peak at 1212 cm^{-1} for tetra oxaspiro linkage in FTIR spectrum, the doublet of = CH_2 (4H) at δ 4.95 in ^{1}H-NMR spectrum and the central spiro-carbon at δ 117.12 in ^{13}C-NMR spectrum confirmed the synthesis of DMTOSU-M1 by TE catalyzed by DCBS, which is not significantly different from DMTOSU-M2 catalyzed by DBTO-CS_2.

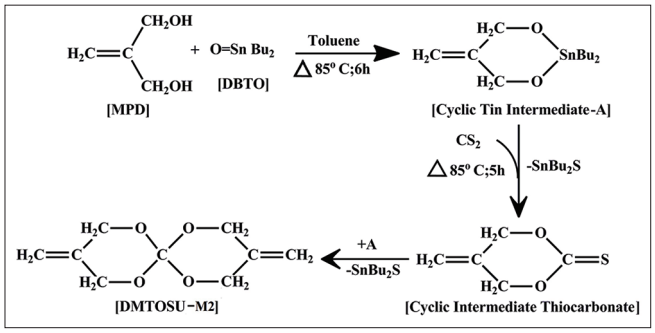


Figure 2: Scheme II – Synthesis of 3,9-Dimethylene-1,5,7,11-tetraoxaspiro[5,5]undecane (M2) catalyzed by dibutyltin oxide-carbon disulfide

Discussion

The reported FTIR and NMR values of DMTOSU by previous researches[28,33-35] were almost similar to DMTOSU-M1 of the present study. Also, there were no significant spectral differences between M1 and M2 in both the FTIR and NMR spectroscopies and hence, the null hypothesis was accepted. This study was successful in synthesizing the double ring-opening DMTOSU through DCBS catalysis. Therefore, DMTOSU can be used as a comonomer in thermo-polymerized DB acrylic resins, which might have less or no polymerization shrinkage.

Due to the pronounced polymerization shrinkage in the thermo-polymerized DB resins and eventual contractile stresses, which lead to various clinical challenges,

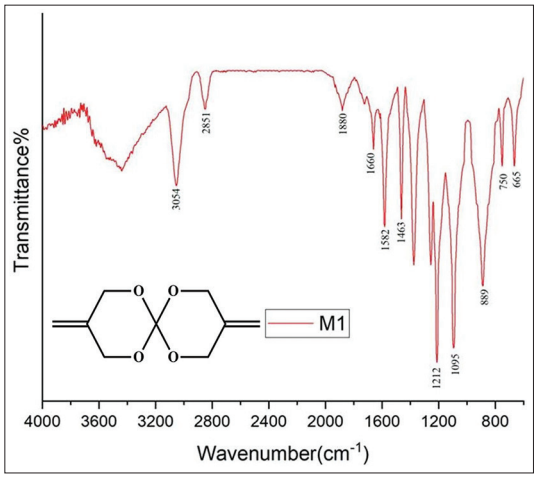


Figure 3: Fourier transform infrared spectrum of 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5,5]undecane-M1

Table 1: Fourier transform infrared spectra of 3,9-Dimethylene-1,5,7,11-tetraoxaspiro[5,5] undecane (M1 and M2)

Functional groups	M1: Wave number (/cm)	M2: Wave number (/cm)
Exocyclic methylene stretch (C-H)	3054	3055
Ring (–CH_2–) symmetric stretch (C-H)	2851	2854
Exocyclic methylene stretch (C=C)	1880	1881
Exocyclic methylene stretch (C=C)	1660	1655
Exocyclic methylene stretch (C=C)	1582	1582
Ring (–CH_2–) symmetric stretch (C-H)	1463	1460
Ester stretch corresponding to strained tetraoxaspiro linkage (O – C –O)	1212	1210
Cyclic ether stretch (C – O – CH_2)	1095	1095
Exocyclic methylene wagging, out of plane deformation (C-H)	889	887
Exocyclic methylene stretch (C-H)	750	746
Exocyclic *cis*-methylene wagging, out of plane deformation (C-H)	665	661

[Downloaded free from http://www.jpbsonline.org on Sunday, June 6, 2021, IP: 106.197.71.153]

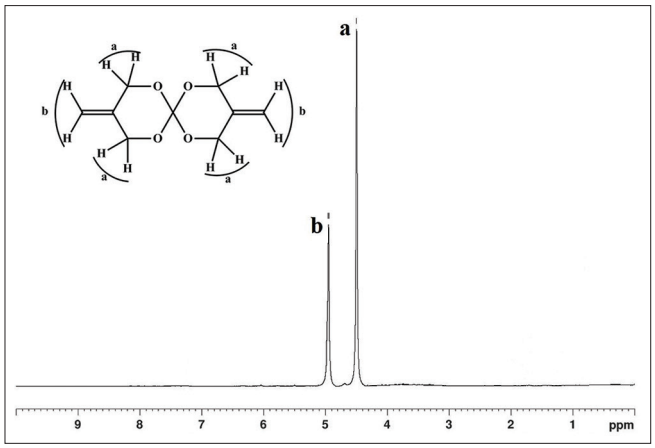


Figure 4: [1]H-nuclear magnetic resonance spectrum of 3,9-Dimethylene-1,5,7,11-tetraoxaspiro[5,5]undecane-M1

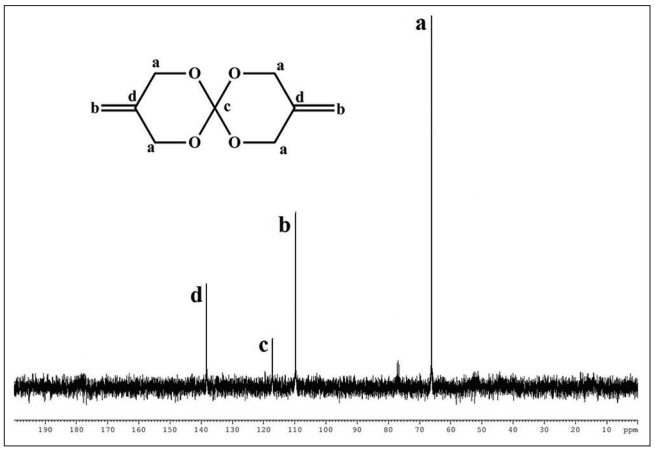


Figure 5: [13]C-nuclear magnetic resonance spectrum of 3,9-Dimethylene-1,5,7,11-tetraoxaspiro[5,5]undecane-M1

Table 2: Nuclear magnetic resonance spectra of 3,9-Dimethylene-1,5,7,11-tetraoxaspiro[5,5] undecane (M1 and M2)

Functional groups	Peak intensity δ (ppm)	
	M1	M2
[1]H-NMR		
A singlet of –OCH_2– (8H)	4.50	4.46
A doublet of =CH_2 (4H)	4.95	4.97
[13]C-NMR		
Central spiro-carbon	117.12	117.31
–OCH_2–	66.53	65.63
=CH_2	109.87	109.14
>C=	138.36	138.36

NMR: Nuclear magnetic resonance

the primary focus turned towards the ring-opening monomers. The polymerization of the SOC monomers occurs through the opening of ring-structures, which in turn leads to volume expansion. DMTOSU, one of the SOC monomers, is selected for this study and it is hardly commercially available. Hence, this mandated the custom synthesis of DMTOSU. Sakai *et al*.[27] synthesized the earliest SOC monomers from the reaction between bis (tributyltin) alkylene glycolates and CS_2. Previous studies have synthesized DMTOSU through DBTO-CS_2 catalytic reaction from MPD.[33,36] Multiple steps, instability of intermediate cyclic tin compounds, and high toxicity of DBTO are the prime disadvantages of this reaction. Synthesis of SOCs by *p*-toluene sulfonic acid catalysts were time consuming. SOC was also synthesized from a diol and thiophosgene in single step. However, thiophosgene's high toxicity risk and transport prohibitions limit this type of reaction.[37] This instigated the search for a novel catalyst with high catalytic potential thereby reducing the synthetic time.

Tributyltin alkoxides were found to be effective in catalyzing TE.[29] Although with limited yields, acrylic esters were effortlessly transesterified. Organotin compounds were not as pragmatic as other catalysts. However, this view was totally changed with the advent of tetraorgano DS or Otera's catalysts. They were now frequently used synthetic catalysts for TE in the organic chemistry and industrial field. DS are air-stable crystalline compounds possessing high melting points and nontoxic for manipulating. Although a large metalloxane core, the DS are soluble in most organic solvents. This is attributed to the eight surface alkyl chains that conceal the inorganic core from the solvent phase. In the presence of nonpolar solvents, TE progresses more smoothly with DS than in polar solvents. This effect is imputed to the special reverse micelle structure exclusive to DS.[38] TE with DS proceeds neutrally in which multitude functional groups of the reactants survive. This is not true for the strong Lewis acid catalysts where the reactants possess acid-sensitive functional groups. TE can be executed with DS under anhydrous conditions to permit the use of moisture-sensitive materials. Therefore, with these advantages, DS are being used in numerous synthetic applications.[32]

In a previous study, tetraorgano DSs were used for TE of ethyl butyrate and 1-heptanol. DCBS possessed higher rate constants and efficient catalytic effect than other DSs. Its catalytic efficiency is ascribed to its unique bidentate coordination properties as Lewis acids. The chlorine atoms induce increased accepting properties when compared to alkoxy or acyloxy DS. DCBS was recovered unchanged after TE; meanwhile, dialkoxy-and diacyloxy-DS became unsymmetrical acyloxy-alkoxy-DS.[39] Hence, in the present study, DCBS was selected as catalyst for TE.

[Downloaded free from http://www.jpbsonline.org on Sunday, June 6, 2021, IP: 106.197.71.153]

TE is preferable over the ester synthesis out of carboxylic acids and alcohols. This is because some sparingly soluble carboxylic acids in organic solvents render the homogeneous esterification difficult. On the other hand, esters (especially methyl and ethyl) are commonly soluble in most of organic solvents and readily available. The ester-to-ester conversion is exclusively useful when the carboxylic acids reactants are labile.[29] Therefore, in the present study, MPD and TEOC (ester of orthocarbonic acid) were used as the parent reactants for the synthesis of DMTOSU.

Conclusion

From the results of the present study, it is concluded that DMTOSU can be synthesized by TE reaction catalyzed by DCBS. The catalytic action of DCBS is a successful alternative to the DBTO-CS_2 catalysis. DMTOSU may be used as a comonomer in DB acrylic resins to offset polymerization shrinkage.

Financial support and sponsorship

Nil.

Conflicts of interest

There are no conflicts of interest.

References

1. Woelfel JB, Paffenbarger GC. Dimensional changes occurring in artificial dentures. Int Dent J 1959;9:451-60.
2. Mowery WE, Burns CL, Dickson G, Sweeney WT. Dimensional stability of denture base resins. J Am Dent Assoc 1958;57:345-53.
3. Woelfel JB, Paffenbarger GC. Method of evaluating the clinical effect of warping a denture: Report of a case. J Am Dent Assoc 1959;59:250-60.
4. Anthony DH, Peyton FA. Dimensional accuracy of various denture base materials. J Prosthet Dent 1962;12:67-81.
5. Goodkind RJ, Schulte RC. Dimensional accuracy of pour acrylic resin and conventional processing of cold-curing acrylic resin bases. J Prosthet Dent 1970;24:662-8.
6. Stafford GD, Bates JF, Huggett R, Handley RW. A review of the properties of some denture base polymers. J Dent 1980;8:292-306.
7. McCabe JF, Wilson HJ. The use of differential scanning calorimetry for the evaluation of dental materials. Part II. Denture base materials. J Oral Rehabil 1980;7:235-43.
8. Picketthg , Appleby RC. A comparison of six acrylic resin processing technics. J Am Dent Assoc 1970;80:1309-14.
9. Umemoto K, Kurata S. Basic study of a new denture base resin applying hydrophobic methacrylate monomer. Dent Mater J 1997;16:21-30.
10. Craig RG, Powers JM. Restorative Dental Materials. 11th ed. St Louis, USA: CV Mosby Co; 2002. p. 647.
11. McCabe JF, Walls AW. Applied Dental Materials. 9th ed. Oxford: Blackwell Publishing Ltd.; 2008. p. 266.
12. van Noort R. Introduction to Dental Materials. 4th ed. St Louis, USA: CV Mosby Co.; 2013. p. 73.
13. Stanford JW, Paffenbarger GC. Processing denture base resins: Heat curing type. J Am Dent Assoc 1956;53:72-3.
14. Woelfel JB, Paffenbarger GC, Sweeney WT. Dimensional changes in complete dentures on drying, wetting and heating in water. J Am Dent Assoc 1962;65:495-505.
15. Woelfel JB, Paffenbarger GC, Sweeney WT. Dimensional accuracy of denture base resins. J Dent Res 1959;38:752.
16. Woelfel JB, Paffenbarger GC, Sweeney WT. Dimensional changes occurring in dentures during processing. J Am Dent Assoc 1960;61:413-30.
17. Lechner SK, Thomas GA. Changes caused by processing complete mandibular dentures. J Prosthet Dent 1994;72:606-13.
18. Carlsson GE. Responses of jawbone to pressure. Gerodontology 2004;21:65-70.
19. Suenaga H, Yokoyama M, Yamaguchi K, Sasaki K. Bone metabolism of residual ridge beneath the denture base of an RPD observed using NaF-PET/CT. J Prosthodont Res 2012;56:42-6.
20. Becker CM, Smith DE, Nicholls JI. The comparison of denture-base processing techniques. Part II. Dimensional changes due to processing. J Prosthet Dent 1977;37:450-9.
21. Laughlin GA, Eick JD, Glaros AG, Young L, Moore DJ. A comparison of palatal adaptation in acrylic resin denture bases using conventional and anchored polymerization techniques. J Prosthodont 2001;10:204-11.
22. Lima AP, Vitti RP, Amaral M, Neves AC, da Silva Concilio LR. Effect of polymerization method and fabrication method on occlusal vertical dimension and occlusal contacts of complete-arch prosthesis. J Adv Prosthodont 2018;10:122-7.
23. MowadeTK, Dange SP, Thakre MB, Kamble VD. Effect of fiber reinforcement on impact strength of heat polymerized methyl polymethacrylate denture base resin: *In vitro* study and SEM analysis. J Adv Prosthodont 2012;4:30-6.
24. Wong DM, Cheng LY, Chow TW, Clark RK. Effect of processing method on the dimensional accuracy and water sorption of acrylic resin dentures. J Prosthet Dent 1999;81:300-4.
25. Begum SS, Ajay R, Devaki V, Divya K, Balu K, Kumar PA. Impact strength and dimensional accuracy of heat-cure denture base resin reinforced with ZrO_2 nanoparticles: An *in vitro* study. J Pharm Bioallied Sci 2019;11:S365-70.
26. Ajay R, Suma K, Ali SA. Monomer modifications of denture base acrylic resin: A systematic review and meta-analysis. J Pharm Bioallied Sci 2019;11:S112-25.
27. Sakai S, Kiyohara Y, Itoh K, Ishii Y. Synthesis of cyclic thioncarbonates and spiroorthocarbonates from bis (tributyltin) alkylene glycolates and carbon disulfide. J Org Chem 1970;35:2347-50.
28. Fu J, Liu W, Hao Z, Wu X, Yin J, Panjiyar A, *et al*. Characterization of a low shrinkage dental composite containing bismethylene spiroorthocarbonate expanding monomer. Int J Mol Sci 2014;15:2400-12.
29. Otera J. Transesterification. Chem Rev 1993;93:1449-70.
30. Endo T, Okawara M. A facile synthesis of spiroorthocarbonates. Synthesis 1984;1984:837.
31. Takata T, Ariga T, Endo T. Cationic ring-opening polymerizations of five-membered spiro orthocarbonates: Unsubstituted and 2,8-diaryl-1,4,6,9-tetraoxaspiro[4.4]nonanes. Macromolecules 1992;25:3829-33.
32. Liu L, Zhang Y, Huang K, Chang W, Li J. 1,3-dichloro-tetra-n-butyl-distannoxane: A new application for catalyzing the direct substitution of 9H-xanthen-9-ol at room temperature. Appl Organomet Chem 2012;26:9-15.
33. Bailey WJ, Endo T. Synthesis of monomers that expand on polymerization. Synthesis and polymerization of 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane. J Polym Sci Pol Chem 1976;14:1735-41.

[Downloaded free from http://www.jpbsonline.org on Sunday, June 6, 2021, IP: 106.197.71.153]

34. Sanda F, Takata T, Endo T. Radical polymerization of 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane. Study of the structure of the polymer and mechanism of polymerization. Macromolecules 1993;26:729-36.
35. Luo Y, Bailey WJ. Polymerization of 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5,5]undecane with dithiols. J Appl Polym Sci 1993;48:1781-93.
36. Thompson VP, Williams EF, Bailey WJ. Dental resins with reduced shrinkage during hardening. J Dent Res 1979;58:1522-32.
37. Sanda F, Takata T, Endo T. Synthesis and radical polymerization of spiroorthocarbonates bearing exo-methylene groups. Macromolecules 1993;26:737-43.
38. Otera J, Ioka S, Nozaki H. Distannoxane as reverse-micelle-type catalyst: Novel solvent effect on reaction rate of transesterification. J Org Chem 1989;54:4013-4.
39. Jousseaume B, Laporte C, Rascle MC, Toupance T. Dichlorodistannoxane transesterification catalysts, pure Lewis acids. Chem Commun (Camb) 2003;9:1428-9.