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Synthesis and Physical Properties of Polyfunctional Methacrylates (Part 4). Synthesis and Physical Properties of Aromatic Dimethacrylate Copolymers

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The eight kinds of aromatic dimethacrylates with different chemical backbones were synthesized and the relationship between the chemical structure and physical properties of these dimethacrylates were investigated.

Key Words: Synthesis, Polyfunctional methacrylates, Physical properties.

INTRODUCTION

Most commercial dental resinous materials have various types of dimethacrylates, such as aromatic, alkylene, and urethane, as major monomeric ingredient. However, the relationship between the chemical structure and the physical properties has not been established.

The previous papers[1,2] described that in order to improve the physical properties of dental resinous materials, two aromatic dimethacrylate monomers containing sulfonyl diphenol backbone, 2,2'-bis(4-methacryloxy phenyl) sulfone (SDMA) and 2,2'-bis(4-methacryloxy ethoxy phenyl) sulfone (MEPS), were synthesized. In that paper, the relationships between their chemical structure and physical properties of these dimethacrylates were investigated. Consequently, the physical properties of dimethacrylate copolymers with methyl methacrylate (MMA) increased by increasing the molar ratio of these dimethacrylates. Thus, it was shown that these dimethacrylates were useful for improving the physical properties of dental resinous materials. However, these dimethacrylates were crystalline solids with a high melting point and showed relatively low solubility with MMA or other conventional dental methacrylate monomers.

We synthesized eight kinds of aromatic dimethacrylates with different backbones, hydroquinone, bisphenol A (isopropylidene diphenol), bisphenol S (sulfonyl diphenol) and biphenyl, and investigated the relationship between the chemical structure and the physical properties of these dimethacrylates.

MATERIALS AND METHODS

1. Preparation of dimethacryloxy phenols

Preparation of 1,4-dimethacryloxy benzene (HQDMA) was carried out by the method of Atsuta, et al.[3]

2,2'-bis(4-methacryloxy phenyl)propane (BPDMA) was prepared according to the method of Atsuta, et al.[4]

Preparation of 2,2'-bis(4-methacryloxy phenyl)sulfone (SDMA) was conducted as previously described.[1]

4,4'-dimethacryloxy biphenyl (DMBP) was prepared by the following method: 29.5 g (0.28 mol) of methacryloyl chloride was added dropwise to a solution of 25 g (0.13 mol) of 4,4'-dihydroxy biphenyl, 28.5 g (0.28 mol) of triethylamine and 400 ml of tetrahydrofuran. The mixture was stirred at a temperature of 0 to 5°C for 3 hrs and filtered to remove the triethylammonium chloride, and the solvent was removed by evaporation. Purification of DMBP was carried out by recrystallization from methanol. A white crystalline material with mp. 136–137°C was obtained.

2. Preparation of dimethacryloxy ethoxy phenols

The synthesis of dimethacryloxy ethoxy phenols was carried out in essentially the same manner. An example is given here using hydroquinone (1,4-dihydroxy benzene) as the substrate.

A solution of 22 g (0.20 mol) of hydroquinone, 18 g (0.45 mol) of sodium hydroxide and 60 ml of water was placed into a three-necked flask and heated at 60°C for 30 min. Then 36 g (0.45 mol) of ethylenechlorohydrin was added dropwise to the mixture, and the mixture was held at 85°C for 6 hrs. After cooling, pale brown crystals were separated and recrystallized with hot water and active charcoal. The white flake crystals, 1,4-bis(2-hydroxy ethoxy)benzene, with mp. 101°C was obtained. 1,4-bis(2-hydroxy ethoxy benzene was esterified by condensation reaction with methacryloyl chloride. 35 g (0.33 mol) of methacryloyl chloride was added dropwise to a solution of 30 g (0.15 mol) of 1,4-bis(2-hydroxy ethoxy) benzene, 34 g (0.33 mol) of triethylamine and 400 ml of N,N-dimethyl folmamide (DMF). During the addition, the reaction mixture was kept at a temperature of 0 to 5°C. After 3hrs, triethylammonium chloride was removed by vacuum filtration. The filtrate was diluted with 500 ml of ethyl acetate and washed several times with 5% HCl solution, and washed with water. After it was dried over anhydrous sodium sulfate, ethyl acetate was removed by evaporation. The yellow oil was purified by recrystallization from methanol to yield white flake crystals with mp. 70°C.

3. Identification of synthesized dimethacrylates

Eight kinds of synthesized aromatic dimethacrylates were identified by infrared, NMR spectra and elemental analysis.

4. Preparation of MMA copolymers

Mixtures of 5, 10, 20, 30, 40 and 50 mol% synthesized dimethacrylates with MMA were prepared as comonomers. Because the solubility limits of SDMA, MEPS, DMBP and DMEBP with MMA were relatively lower than the others, the comonomers with maximum concentration, 10, 40, 10 and 40 mol% were prepared, respectively.

Copolymerization was carried out with 0.5wt% of benzoyl peroxide (BPO) at 60°C for 12 hrs and 120°C for 10 hrs.

5. Physical properties

All specimens, except for specimens for determining water sorption, were tested in

both the dry and wet states to evaluate the effect of water sorption on the physical properties of copolymers. The dry specimens were stored in a desiccator at room temperature for 24 hrs and the wet specimens were immersed in distilled water at 37°C for one month.

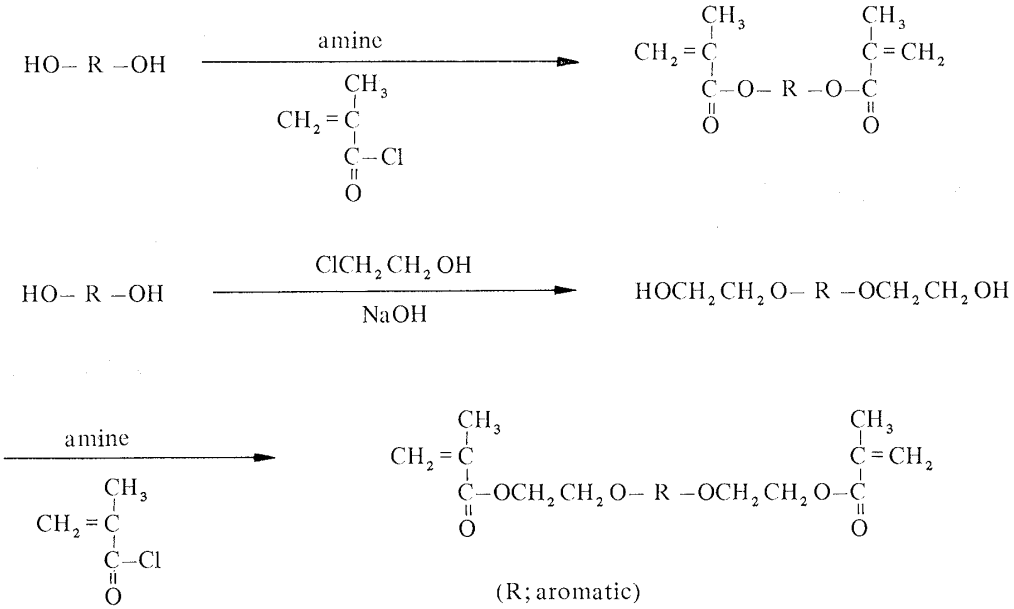
Specimens for compressive strength and modulus of elasticity were $5\phi \times 7$ mm cylinders. Measurements of compressive strength were made on a universal testing machine at a crosshead speed of 1 mm/min. Because the cylindrical specimens showed large plastic deformations by compressive stress, the values of proportional limit were calculated as compressive strength.

Knoop hardness was measured on cylindrical specimens ($10\phi \times 10$ mm) with 100 g load.

Amounts of water sorption were determined on disc specimens ($10\phi \times 0.5$ mm). After vacuum drying, disc specimens were immersed in distilled water at 37°C for one month, and then the amounts of water sorption were calculated as the gain weight per centimeters of surface areas.

RESULTS

The eight kinds of aromatic dimethacrylates were prepared by the following schemes:



The structure and properties of these dimethacrylates are listed in Table 1. Table 2 contains the infrared and NMR spectra assignments.

On comparing the melting points of these dimethacrylates, it was found that in every case dimethacryloxy phenols had higher melting points than the dimethacryloxy ethoxy derivatives of the corresponding phenols.

The relationship between the compressive strength and the concentration of these dimethacrylates is shown in Figs. 1 and 2, and the modulus of elasticity is shown in Figs. 3 and 4. Within the concentration range studied, compressive strength and modulus of elasticity rose by increasing the concentration of dimethacrylates. Dimethacrylates containing bisphenol A and bisphenol S backbones gave relatively higher compressive strength

Table 1 Structure and properties of synthesized dimethacrylates

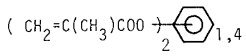
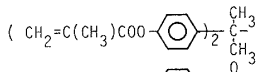
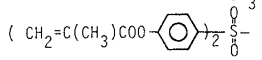
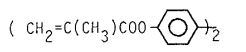
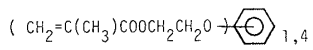
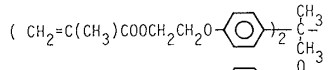
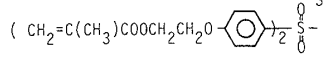
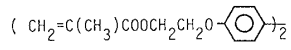
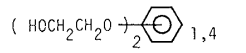
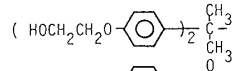
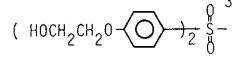
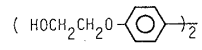
Structure	Abbreviation	Molecular weight	Melting point	Elementary analyses Calc'd(%) C	Calc'd(%) H	Found(%) C	Found(%) H
	HQDMA	246.3	88-89°C	68.28	5.73	---	---
	BPDMA	364.4	72°C	75.80	6.64	---	---
	SDMA	386.4	151-152°C	62.17	4.70	61.97	4.69
	DMBP	322.4	136-137°C	74.52	5.63	74.69	5.49
	DMEBZ	334.3	70°C	64.66	6.63	65.27	6.39
	MEPP	452.6	42-43°C	71.65	7.13	71.65	7.16
	MEPS	474.5	87-88°C	60.75	5.52	61.20	5.40
	DMEBP	410.5	74°C	70.22	6.38	70.65	6.22
	DHEBZ	198.2	101°C				
	DHEPP	316.4	107-109°C				
	DHEPS	338.3	180-182°C				
	DHEBP	274.3	212-215°C				

Table 2 Infrared and NMR spectra assignments of synthesized dimethacrylates.

Dimethacrylate	NMR chemical schift (ppm) * =CH_2	aromatic	-CH_2-	-CH_3	IR absorption bands(cm^{-1}) ** C=O	C=C	SO_2
HQDMA	5.85(2H) 6.50(2H)	7.30(4H)	---	2.10(6H)	1730	1640	---
BPDMA	5.76(2H) 6.38(2H)	6.91-7.61 (8H)	---	2.08(6H) 1.68(6H)	1720	1645	---
SDMA	5.80(2H) 6.35(2H)	7.25-8.15 (8H)	---	2.05(6H)	1730	1640	1320
DMBP	5.70(2H) 6.30(2H)	7.00-7.70 (8H)	---	2.05(6H)	1730	1640	---
DMEBZ	5.75(2H) 6.31(2H)	7.05(4H)	4.10-4.90 (8H)	2.05(6H)	1720	1645	---
MEPP	5.45(2H) 6.02(2H)	6.45-7.20 (8H)	3.80-4.45 (8H)	1.80(6H) 1.50(6H)	1710	1640	---
MEPS	5.55(2H) 6.06(2H)	6.60-8.00 (8H)	3.90-4.60 (8H)	1.85(6H)	1720	1640	1320
DMEBP	5.55(2H) 6.17(2H)	6.80-7.80 (8H)	4.00-4.75 (8H)	1.90(6H)	1720	1640	---

* run in $CDCl_3$

** KBr

and modulus of elasticity.

Knoop hardness of these dimethacrylate copolymers are shown in Figs. 5 and 6. Copolymers showed an increase in Knoop hardness with increasing dimethacrylate content.

The relationship between the amounts of water sorption and the concentration of

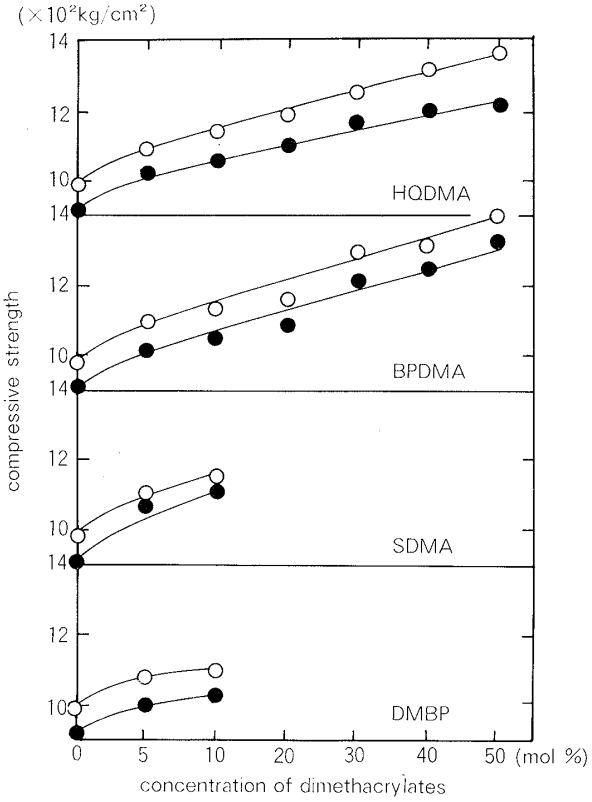


Figure 1 Relationship between the compressive strength and the concentration of synthesized dimethacrylates (○: Dry, ●: Wet)

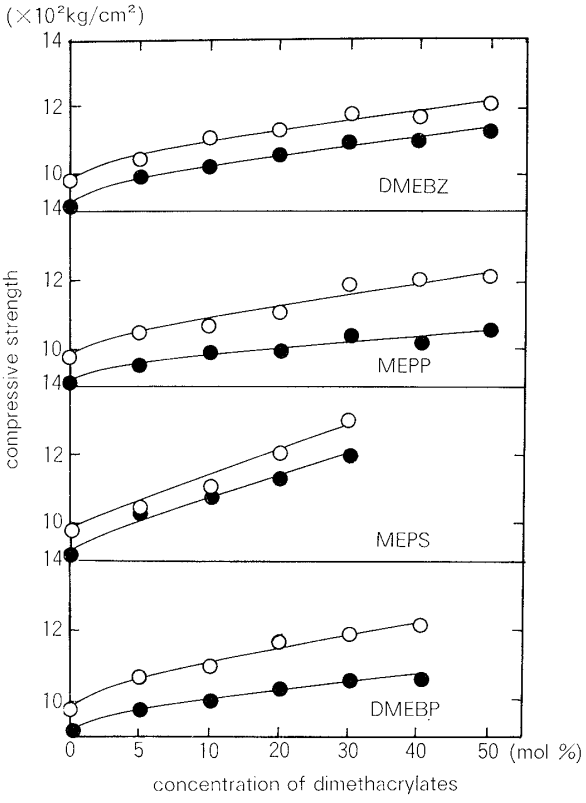


Figure 2 Relationship between the compressive strength and the concentration of synthesized dimethacrylates (○: Dry, ●: Wet)

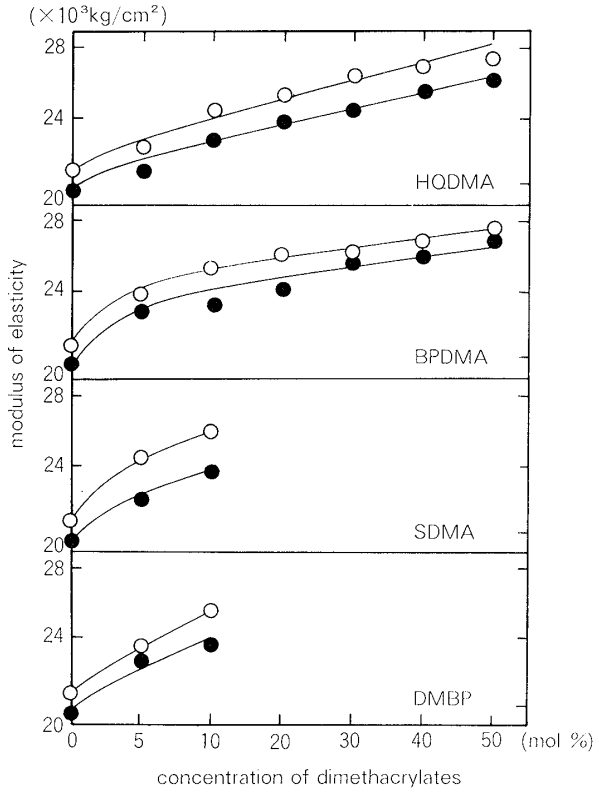


Figure 3 Relationship between the modulus of elasticity and the concentration of synthesized dimethacrylates (○: Dry, ●: Wet)

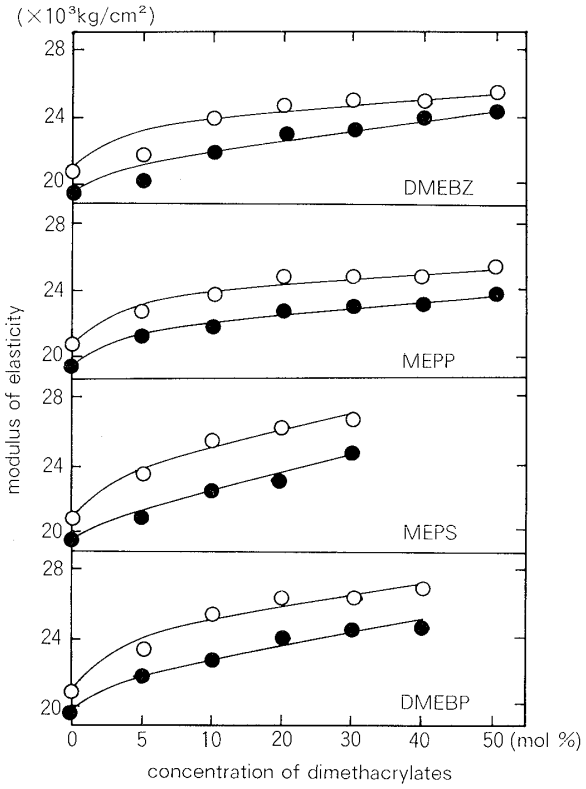


Figure 4 Relationship between the modulus of elasticity and the concentration of synthesized dimethacrylates (○; Dry, ●: Wet)

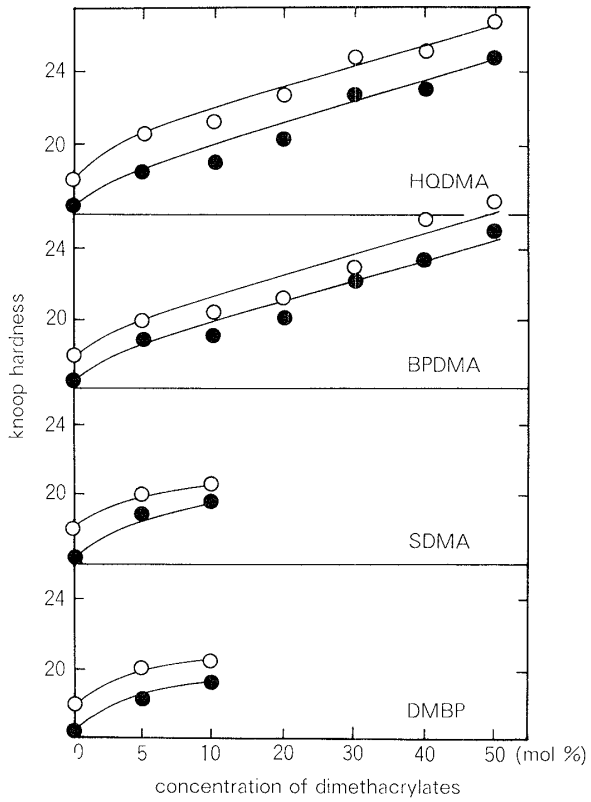


Figure 5 Relationship between the knoop hardness and the concentration of synthesized dimethacrylates (○: Dry, ●: Wet)

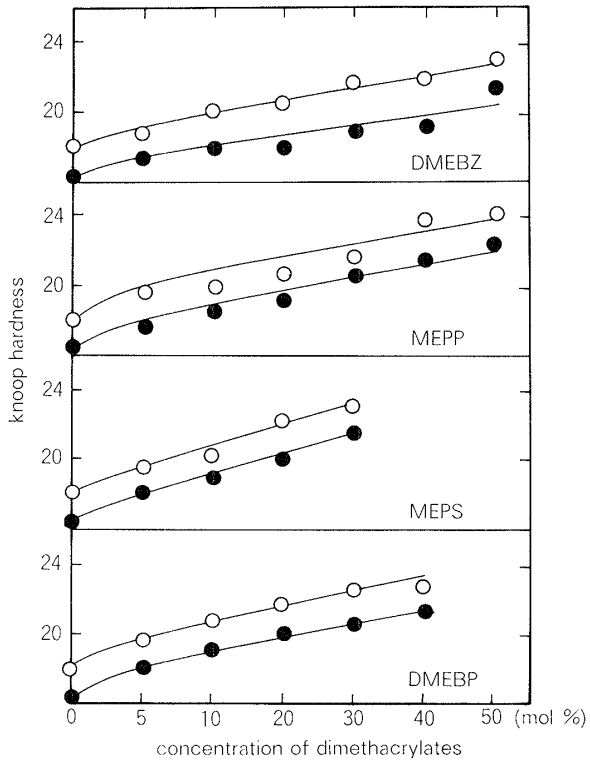


Figure 6 Relationship between the Knoop hardness and the concentration of synthesized dimethacrylates (○: Dry, ●: Wet)

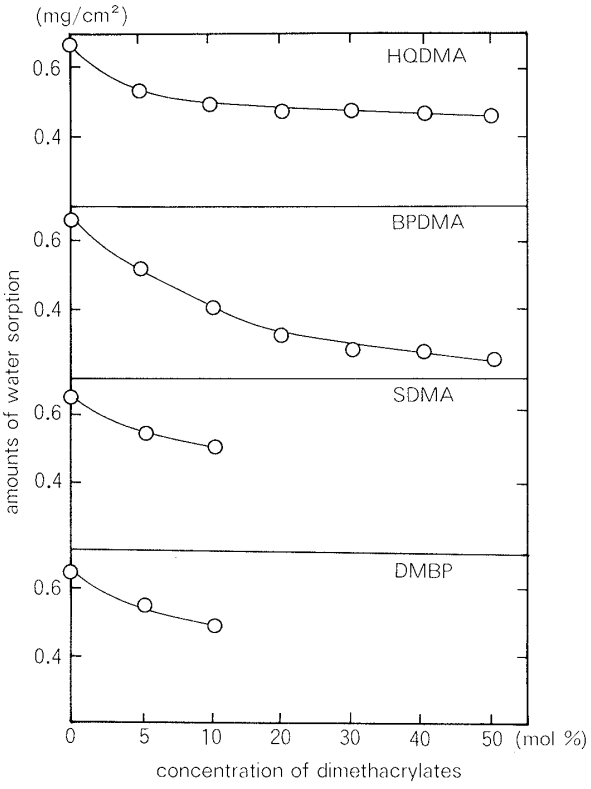


Figure 7 Relationship between the amounts of water soorption and the concentration of synthesized dimethacrylates

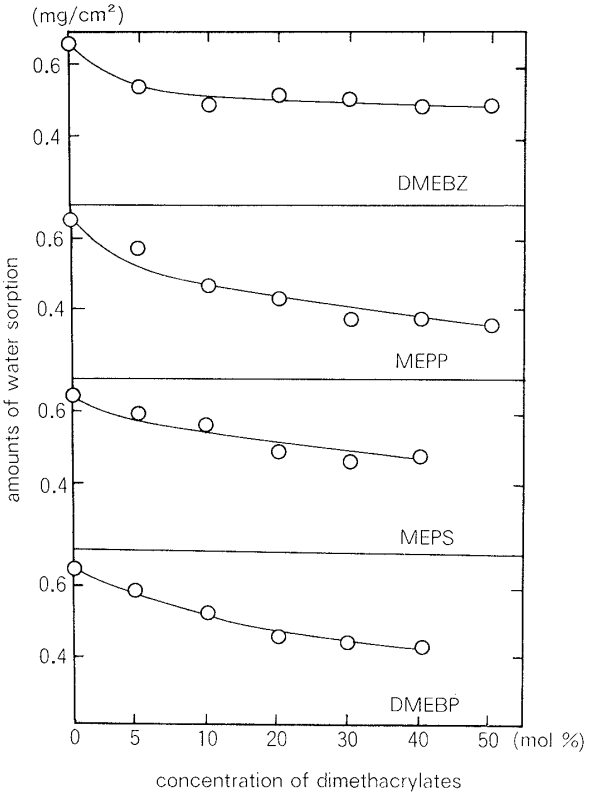


Figure 8 Relationship between the amounts of water sorption and the concentration of synthesized dimethacrylates

dimethacrylates is shown in Figs. 7 and 8. With increasing dimethacrylate concentration, the amounts of water sorption of copolymers decreased. Dimethacrylates containing bisphenol A and biphenyl backbones gave relatively lower water up-take

On comparing the physical properties of these dimethacrylate copolymers, it was found that dimethacryloxy ethoxy derivatives had relatively lower mechanical properties than the corresponding dimethacryloxy phenols. Mechanical properties of these dimethacrylate copolymers slightly decreased by immersion in distilled water at 37°C for one month.

DISCUSSION

Dimethacrylate monomers are now widely used as major monomeric ingredients of dental resinous mateirals. A number of dimethacrylate monomers containing different chemical backbones have been reported during the past twenty years. However, the relationship between the chemical structure and the physical properties of these dimethacrylates have not been established.

The purpose of our study was to investigate the relationship between the chemical structure of polyfunctional methacrylate molecules and their physical properties. Because we expected that the physical properties of dental resinous materials could be improved by the introduction of aromatic groups into the backbone, we synthesized the eight kinds of dimethacrylates with different aromatic groups into the backbone.

As shown by the results in this study, these aromatic dimethacrylates improved the physical properties of MMA copolymers. Dimethacrylates containing bisphenol A and bisphenol S backbones yielded higher physical properties than those containing biphenyl and hydroquinone backbones. Therefore, the introduction of bisphenol A and bisphenol S backbones are significantly useful for improving the physical properties of dental resinous materials.

These crystalline dimethacrylate monomers are relatively easy to purify by recrystallization. However, these aromatic dimethacrylates except for MEPP had a relatively higher melting point and lower solubility for conventional dental monomers. Introduction of alkylene groups into the backbone reduced the melting point, and improved the solubility of aromatic dimethacrylates. It has been reported that dimethacrylates containing $(CH_2)_n$ groups in the backbone yields generally more desirable physical properties than those containing $(CH_2CH_2O)_n$ groups.[5]

On comparing the physical properties of these aromatic dimethacrylate copolymers, it was found that the introduction of alkylene groups into the backbone slightly decreased the mechanical strength (such as compressive strength, modulus of elasticity and Knoop hardness) and slightly increased the amounts of water sorption. However, the physical properties of dimethacryloxy ethoxy derivatives containing bisphenol A and bisphenol S are high enough for use as dental monomers. Therefore, it is considered that dimethacryloxy alkyloxy bisphenol A and dimethacryloxy alkyloxy bisphenol S are the most desirable dimethacrylate monomers for improving the physical properties of dental resinous materials.

CONCLUSIONS

In order to improve the physical properties of dental resinous materials, the eight kinds of aromatic dimethacrylates were synthesized and the relationships between the chemical structure and physical properties of these dimethacrylates were investigated.

Mechanical properties (compressive strength, modulus of elasticity and Knoop hardness) of MMA copolymers increased by increasing the concentration of dimethacrylates.

The physical properties of dimethacryloxy phenols were relatively higher than those of dimethacryloxy ethoxy derivatives for corresponding phenols.

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Ni-43.5% Ti 超弾性合金鋳造体の疲労特性

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**大阪歯科学院専門学校

Ni-43.5% Ti 合金をアルゴンアーク溶解加圧鋳造機により，リン酸塩系埋没材鋳型に鋳造した。鋳造体は片持ち曲げ試験において超弾性を示した。本合金を新しいキャスト・クラスプ用合金として評価するために，疲労特性を検討した。疲労試験は片持ち片振り繰返し曲げ方式の試作試験機で行った。本合金の耐疲労性は，曲げ特性を考慮した時，比較対照とした Co-Cr 合金および Type IV 金合金より優れていることが知られた。

Pd を含む市販歯科用金合金の等温時効硬化

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パラジウムを含有する市販歯科用 14 K，16 K 金合金の等温時効による硬さの変化とその原因機構について，電気抵抗測定，硬さ試験，X線回折，電子顕微鏡直接観察，制限視野電子線回折によって検討した。

時効硬化は準安定相である AuCu I′ 規則格子の形成に伴う整合ひずみによって生ずる。AuCu I′ 規則相は反応の進行とともにひずみを解放するため双晶化するが，これによる過時効軟化は顕著ではない。過時効軟化は平衡相 AuCu I 規則格子と Ag-rich α_2 相の二相分離が結晶粒界から起こることによって生じ，その原因はこれら二相によって形成されたラメラ構造の界面が非整合になるためであることが解った。

種々な溶融方法による歯科用 Ni-Cr 系合金鋳造体中の酸素および窒素量

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種々な溶融方法を用いて鋳造した 3 種類の市販 Ni-Cr 系合金と純 Ni の鋳造体（研磨後）中に含まれる酸素と窒素の定量を行い，両者の量に及ぼす溶融方法および合金成分の影響について検討を加えた。比較した溶融方法はアルゴンガス中高周波，大気中高周波，2 種類のアルゴンアーク（アルゴンガス置換とアルゴンガス吹き付け），酸素―プロパン混合ガスを用いたトーチによる溶融の計 5 種類とした。アルゴンガス吹き付けによるアーク溶融は他の溶融方法 4 種類に比べて有意にガスの吸収を引き起こし，他の溶融方法ではその間に有意な差は認められなかった。この影響は特に，Cr, Si あるいは Mn をあまり多く含まない合金に対し顕著に示されていた。さらにこの合金において，アルゴンガス吹き付けによるアーク溶融を用いた鋳造体の内部には多くのポロシティーが確認された。一方，硬さに対しては有意な影響は認められなかった。

多官能性メタクリレートの合成と物性について（その 4）芳香族系ジメタクリレートの合成と物性について

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歯科用レジン材料の物性向上を目的として，多官能性メタクリレートの構造と物性との相関を検討中である

が，前報では，分子中心骨格がビスフェノールS型のジメタクリレートの合成とMMA共重合体の物性について検討を加えた。その結果，芳香族系の導入が共重合体の物性向上に有効であることが判明した。今回は，分子中心骨格に各種の芳香族系を有するジメタクリレートの分子構造と物性との相関を検討する目的で，中心骨格にビスフェノールA，ビスフェノールS，ハイドロキノン，ビフェニル構造を有し，鎖長の異なる8種のジメタクリレートを合成し，MMA共重合体の物性を測定した。その結果，ビスフェノールS，ビスフェノールAを中心骨格に有するジメタクリレートが，総体的に良好な物性を示し，歯科用メタクリレートモノマーとしての有効性が示唆された。

超微粒子フィラー配合コンポジットレジンおよび支台築造用コンポジットレジンの細胞毒性 (in vitro)

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超微粒子フィラー配合コンポジットレジン3製品と支台築造用コンポジットレジン4製品の硬化試料のHeLa S3細胞に対する細胞毒性を調べるために，in vitro環境下で細胞コロニー形成法を駆使して実験を行った。2週間の単位浸漬期間を合計6週間にわたって，口腔内の動的環境のシミュレーションを目ざした旋回投入浸漬を続け，各時期の浸漬液を実験に用いた。その結果，テストした全材料で初期に浸漬液の濃度があがると中等度から強い細胞毒性を示した。しかし，浸漬4週目，6週目においてはその細胞毒性はほとんど消失し去った。この結果は同時にテストした従来型のConciseと酷似していたし，既にテストした他の従来型製品とも軌を一にするものであった。以上の実験結果はテストした2種類のコンポジットレジンが細胞に対して従来型製品ときわめてよく似た影響を及ぼすことを示している。

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クロルヘキシジン塩酸塩を配合した抗菌性根管充填用シーラーに関する研究

第2報　抗菌性の検討およびその臨床応用に関す遠隔成績について

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クロルヘキシジン塩酸塩の配合による，根管充填用シーラーへの抗菌性の付与を目的とした本研究の第一報において，ベースとなるシーラーの材料学的な検討がなされ，優れた物性を示すように組成が決定された。本報の前半では，この組成にクロルヘキシジン塩酸塩を配合した試作シーラー（K-20）に関して，硬化物からの有効成分の溶出，口腔内細菌に対する抗菌性およびその経時的変動についての吟味が行われ，さらに動物実験によって安全性が確かめられた。また後半では，こうして抗菌性と安全性が確認されたK-20を実際の症例に適用し，その遠隔成績について調査がなされた。これらの結果より，強力で確実な抗菌性と安全性を併せもつK-20は，その臨床応用に際して不快な副作用を伴うこともなく，予後の調査でも従来の報告に比較して，優るとも劣らない成績を示した。これより，抗菌性を備えたK-20の使用は，根管充填の成功に寄与するものであると考えられる。