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Syntheses of *O*-Methacryloyl-*N*-Acyl Tyrosines and Their Adhesiveness to Un-etched Human Dentin

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O-Methacryloyl-*N*-acyl tyrosines (MAATY) having acyl groups with the various chain length were synthesized and the strength of bonding agents, consisting of MAATY as an adhesive monomer, to unetched human dentin was studied to elucidate the relationship between the molecular structure of MAATY and its adhesive characteristics. Increasing the flexibility of the carboxyl group of tyrosine favors the interaction with the tooth substrate, causing strict bonding. Also, the properties of the neighboring carboxyl group, i. e., steric hindrance and hydrophobicity, hydrophobic-hydrophilic balance in the monomer, and shrinkage of the monomer at copolymerization, are considered important. Especially, steric hindrance of the substituted group neighboring the carboxyl group of tyrosine would play an extremely important role in the adhesion of *O*-methacryloyl-*N*-octanoyl tyrosine. The maximum tensile bond strength was obtained with a bonding agent consisting of *O*-methacryloyl-*N*-hexanoyl tyrosine (15 mol%) and hydroxyethyl methacrylate (85 mol %), and the strength (4.75 MPa) was the maximum in all methacrylates with phenylalanine as a bone structure.

Key words: Tyrosine derivative, Steric hindrance, HLB value

INTRODUCTION

All commercial bonding agents currently have extremely limited adhesive strength to unetched teeth. Therefore, etching of the enamel and dentin with acids is essential in clinical practice[1~3]. However, etching the tooth structure causes undesirable effects and if possible, should be avoided. It is therefore quite important to develop a bonding agent having favorable bonding characteristics without etching.

Suzuki *et al.*[4,5] have synthesized various adhesive monomers derived from α-amino acids, and found that *N, O*-dimethacryloyl tyrosine (DMTY), which is derived from tyrosine, has favorable adhesive characteristics to unetched human dentin. The polymer of DMTY, which is a bifunctional monomer, has a crosslinkage structure. Therefore, it is considered that the mobility of the carboxyl group, which is desirable for the formation of hydrogen and/or coordinate bonds with tooth substrates, is restricted. Also, the neighboring structure of the carboxyl group is important. If various substitutional groups can be introduced into the amino group of tyrosine, which is in the neighborhood of the carboxyl group, it would help elucidate the favorable neighboring structure of carboxyl group received for their bonding.

O-Methacryloyl-*N*-acyl tyrosines (MAATY), having a methacryloyl group introduced into the position of the phenolic hydroxyl group of tyrosine and acyl groups of various chain lengths introduced into the position of amino group of tyrosine, were synthesized. Their adhesive properties for unetched human dentin were studied to elucidate the relationship between the molecular structure of the adhesive monomer and its bonding to unetched human dentin.

MATERIALS AND METHODS

1. Syntheses of MAATY

General methods for the syntheses of MAATY

MAATY were synthesized as described below.

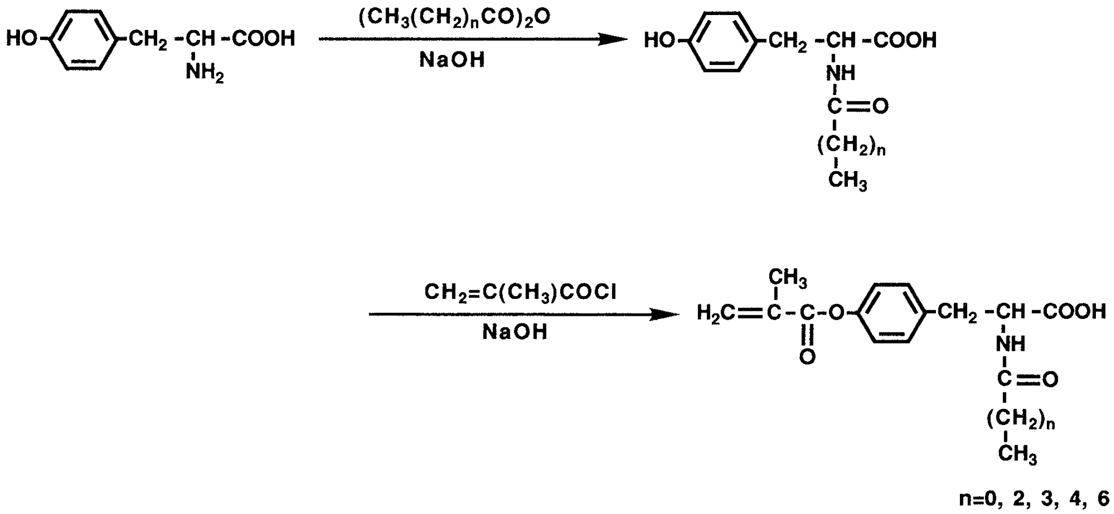
N-acyl tyrosines were synthesized from L-tyrosine and various anhydrides of acids having alkyl groups corresponding to *N*-acyl groups of various chain lengths on MAATY were added under alkaline conditions (pH=9). MAATY were then synthesized from these *N*-acyl tyrosines and methacryloyl chloride (MACl), also under alkaline conditions (pH=9~11) at 0~4°C.

Syntheses of N-acyl tyrosines (Acylation of amino group on L-tyrosine using anhydrides)

L-Tyrosine, 23 g (0.127 mol), was placed into a 500 ml three-necked round bottom flask equipped with a condenser and two funnels. After dissolving L-tyrosine in 240 ml of 1N-NaOH, 0.152 mol (1.2 times to L-tyrosine) of an anhydride (acetic, n-butyric, n-valeric, n-hexanoic or n-octanoic anhydrides) was added dropwise with stirring. The pH of the solution was maintained at 7~9 by adding 4N-NaOH at the same time. After adding the anhydrides, the solution was left for 1 hr. Thereafter, 6N-HCl was dropped into the solution while stirring until the pH reached 1~2.

In the reaction system of L-tyrosine and acetic anhydride, white crystals of *N*-acetyl tyrosine gradually precipitated in the solution. After separating the crystals, the solution was passed through filter paper. The white crystals were dried in vacuo at room temperature. Yield: 25.0 g (88 mol% to L-tyrosine).

In the reaction system of L-tyrosine and n-butyric anhydride or n-valeric anhydride, the reaction solution settled into two layers (oil and water phases). The two phases were collected with a separating funnel. The oil phase was washed with 1N-HCl, and white



Scheme 1 Syntheses of *O*-methacryloyl-*N*-acyl tyrosines (MAATY)

crystals of *N*-acyl tyrosines (*N*-butyryl or *N*-valeryl tyrosine) gradually precipitated. After separating the crystals, the reaction solution was passed through filter paper. The white crystals were dried in vacuo at room temperature. Yield: 29.3 g *N*-butyryl tyrosine (92 mol% to L-tyrosine); 30.3 g *N*-valeryl tyrosine (90 mol% to L-tyrosine).

In the reaction system of L-tyrosine and n-hexanoic or n-octanoic anhydride, the reaction solution settled into two layers. The oil and water phases were collected with a separating funnel. *N*-Acyl tyrosine (*N*-hexanoyl and *N*-octanoyl tyrosines) was isolated by column chromatography, from the oil phase containing *N*-acyl tyrosine and the corresponding acid as co-product. The separation conditions were as follows. Packing, silica gel*; Eluent, benzene: methyl alcohol: acetic acid=48: 8: 8. Yield: 19.0 g *N*-hexanoyl tyrosine (54 mol% to L-tyrosine); 26.7 g *N*-octanoyl tyrosine (68 mol% to L-tyrosine).

Syntheses of MAATY (Acylation of the hydroxyl group on N-acyl tyrosines using MACl)

N-Acyl tyrosines, 0.064 mol, were placed in a 300 ml three-necked round bottom flask fitted with a condenser and two funnels. After dissolving *N*-acyl tyrosines in 60 ml of 2N-NaOH, the solution was cooled to 0～4°C in an ice-salt bath. Thereafter, 6.2 ml of MACl was added dropwise with stirring into the solution, and the pH was maintained at 9～11 by simultaneously adding 4N-NaOH. Thereafter, the solution was left for 1 hr, then the pH was adjusted to about 1 using 6N-HCl, and MAATY as white crystals precipitated. The crystals separated by filtration were recrystallized with ethyl acetate and dried in vacuo at room temperature. Yield: 12.6 g (68 mol% to *N*-acetyl-L-tyrosine) *O*-methacryloyl-*N*-acetyl-L-tyrosine (MATY); 4.3 g (21 mol% to *N*-butyryl-L-tyrosine) *O*-methacryloyl-*N*-butyryl-L-tyrosine (MBTY); 8.8 g (41 mol% to *N*-valeryl-L-tyrosine) *O*-methacryloyl-*N*-valeryl-L-tyrosine (MVTY); 18.0 g (81 mol% to *N*-hexanoyl-L-tyrosine) *O*-methacryloyl-*N*-hexanoyl-L-tyrosine (MHTY); 10.8 g (45 mol% to *N*-octanoyl-L-tyrosine) *O*-methacryloyl-*N*-octanoyl-L-tyrosine (MOTY). These MAATY were recrystallized two or three times with ethyl acetate, and their structure and purity were determined by elementary analysis (E. A.)**, thin-layer chromatography (TLC)#, infra-red spectroscopy (IR)## and nuclear magnetic resonance spectroscopy (NMR)@.

2. Preparation of bonding agents

The bonding agent, containing MAATY, was composed of Liquids A and B. Liquid A: MAATY and hydroxyethyl methacrylate (HEMA) as a comonomer (total monomer weight 1 g) were dissolved in 1 g of ethyl alcohol, and 10 mg of benzoyl peroxide (BPO) as a initiator was also added. Liquid B: 10 mg of the sodium salt of benzenesulfinic acid (BSANa) as an activator of polymerization was dissolved in 1 g of ethyl alcohol. An equal volume of Liquid A and B was mixed at the time of application onto the dentinal surface.

3. Preparation of specimens and the measurement of tensile bond strength

The labial surface of freshly extracted human permanent molars, stored in distilled water, was flattened with emery paper (JIS #600), and dried in air for 10 s. A polyethylene ring, 3.8

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* Kieselgel 60, E. Merck, Darmstadt, Germany

** MT-5, Yanako, Kyoto, Japan

\# Iatroscan TH-10 TLC/FID analyzer, Iatron laboratories, Inc., Tokyo, Japan

\## IR-810, Japan spectroscopic co., Ltd., Tokyo, Japan

@ Varian VXR-500, Varian instruments Ltd., CA, USA mm inside diameter, was fixed on the flattened dentin surface with doublesided tape. The bonding agent containing MAATY, was applied onto the dentinal surface inside the polyethylene ring with a sponge pellet and dried in air for 15 s. Thereafter, a composite resin[@@] was applied by its own weight. Specimens were stored in water at 37°C for 24 hr.

Tensile bond strength was measured by a universal testing machine[$] with a cross-head speed of 2 mm/min. Each experiment included 12～20 determinations. The data were evaluated by the analysis of variance and Scheffe's test for multiple comparisons between means at the $p=0.05$ level of significance.

4. *Measurement of polymerization shrinkage*

MAATY, 5 mol%, HEMA, 95 mol%, and 0.2 wt/wt% to monomer total weight of BPO as the initiator were placed in a polymerization ampule that was sealed with an oxygen torch under reduced pressure. Polymerization proceeded in a constant temperature water bath, electrically heated and controlled at 60 ±0.02°C for 24 hr. After complete polymerization, the monomer-initiator mixture converted to a solid of which, the shape was controlled by that of the ampule. The solid was removed from the ampule and its density was determined by directly comparing of the weight of equal volumes of solid and water at 4°C. Polymerization shrinkage of each polymerization system of MAATY with HEMA was determined by comparing the density of polymerized solid with that of monomer mixture determined using a micropycnometer.

5. *Measurement of pKa*

MAATY, 0.1 mmol, were dissolved in 1 ml of 1N-NaOH and each was diluted with distilled water to 20 ml. The pH change at the neutralization titration of the alkaline solution of MAATY with 0.3N-HCl was determined using pH meter[$$]. The pKa of MAATY were determined from the titration curve.

RESULTS

Elementary analyses and ^{1}H-NMR spectra of MAATY and their assignments are shown in Table 1 and Fig. 1. These results indicated that MAATY were obtained in high purity.

Table 1 Elementary analyses of *O*-methacryloyl-*N*-acyl tyrosines (MAATY)

MAATY		C (%)	H (%)	N (%)
O-methacryloyl-*N*-acetyl tyrosine (MATY)	Obs'd :	60.97	5.85	4.67
	(Calc'd) :	(61.85)	(5.88)	(4.81)
O-methacryloyl-*N*-butyryl tyrosine (MBTY)	Obs'd :	63.42	6.64	4.39
	(Calc'd) :	(63.94)	(6.63)	(4.39)
O-methacryloyl-*N*-valeryl tyrosine (MVTY)	Obs'd :	64.62	6.98	4.19
	(Calc'd) :	(65.05)	(6.67)	(4.21)
O-methacryloyl-*N*-hexanoyl tyrosine (MHTY)	Obs'd :	65.28	7.28	4.00
	(Calc'd) :	(65.69)	(7.25)	(4.03)
O-methacryloyl-*N*-octanoyl tyrosine (MOTY)	Obs'd :	67.23	7.86	3.67
	(Calc'd) :	(67.18)	(7.78)	(3.73)

[@@] Clearfil F-II, Kuraray, Okayama, Japan
[$] Autograph DCS-2000, Shimadzu Corp., Kyoto, Japan
[$$] F-8DP, Horiba, Kyoto, Japan

The tensile bond strength of MAATY-hydroxyethyl methacrylate (HEMA) bonding systems to the unetched human dentin (#600) is shown in Table 2. The monomer feed of MAATY had an apparent influence on the tensile bond strength. The optimum of all MAATY-HEMA bonding systems except *O*-methacryloyl-*N*-acetyl tyrosine (MATY), which was very slightly soluble in HEMA, appeared unrelated to the chain length of the *N*-acyl group in MAATY, at about 15 mol% in the monomer feed. The optimum tensile bond

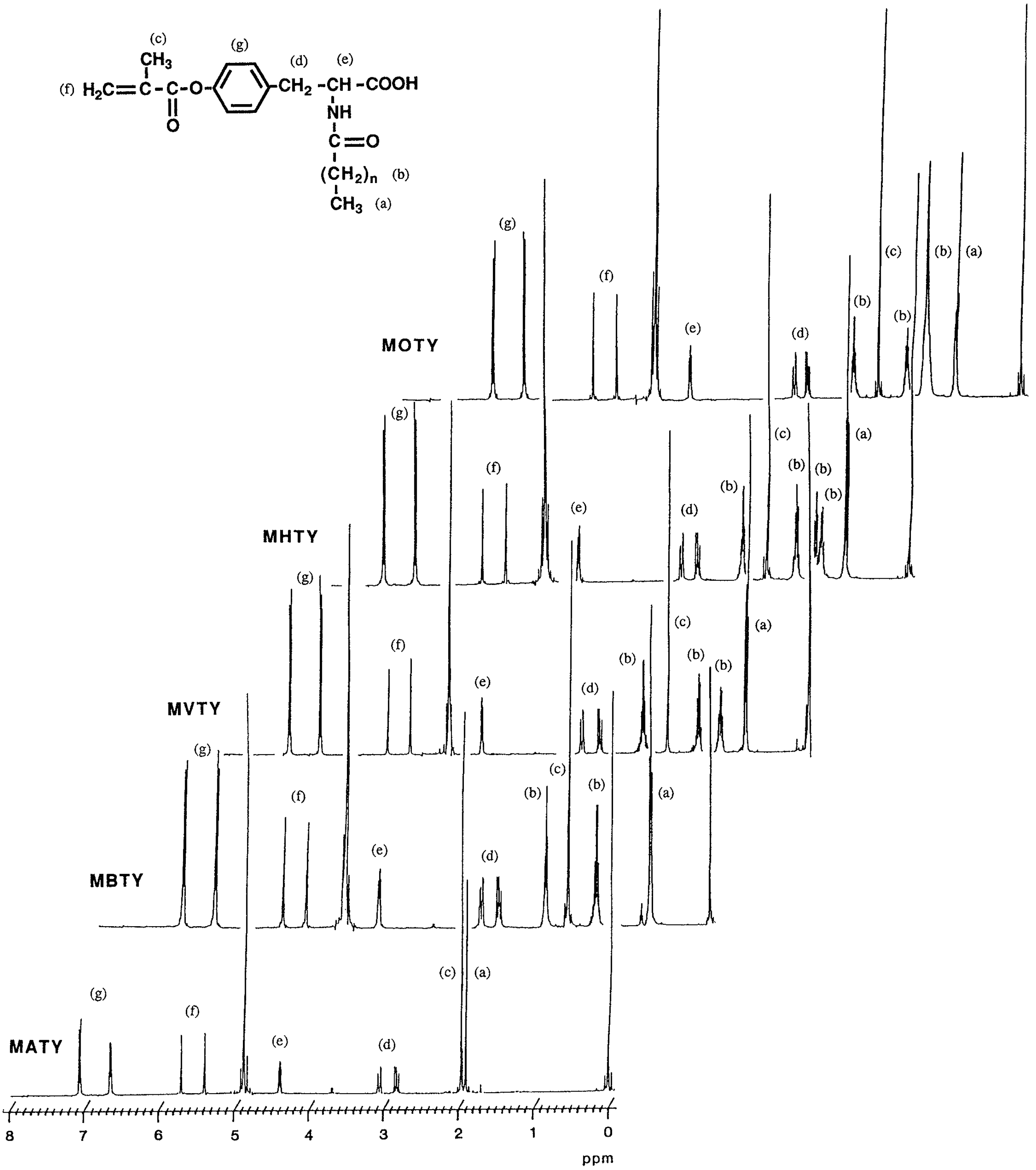

Fig. 1 ^{1}H-NMR spectra of MAATY at 500MHz in D_2O+NaOD at room temperature.

strength of each MAATY-HEMA complex tended to become stronger with increasing carbon numbers in the *N*-acyl group of MAATY. The complex of *O*-methacryloyl-*N*-hexanoyl tyrosine (MHTY ; the carbon number of *N*-acyl group, n=6) with HEMA peaked and showed maximal tensile bond strength in all MAATY-HEMA systems. The tensile strength decreased in *O*-methacryloyl-*N*-octanoyl tyrosine (MOTY ; n=8), which has a longer acyl chain. The optimal tensile bond strength of the MOTY-HEMA system was weaker than those of *O*-methacryloyl-*N*-butyryl tyrosine (MBTY ; n=4), *O*-methacryloyl-*N*-valeryl tyrosine (MVTY ; n=5) and MHTY (n=6).

The polymerization shrinkage of each copolymerization system determined based upon the bulk copolymerization of MAATY (5 mol%) with HEMA (95 mol%) and pKa of carboxyl group on MAATY, was plotted against the carbon number of the *N*-acyl chain of MAATY as shown in Fig. 2. The shrinkage of each copolymerization system tended to decrease with the increasing carbon number of the *N*-acyl chain. On the other hand, the pKa of the

Table 2 The effect of the molar ratio of MAATY in MAATY-HEMA bonding systems on the adhesive strength to unetched human dentin (#600)

Molar ratio of MAATY	Tensile bond strength (MPa)				
	MAATY				
	MATY	MBTY	MVTY	MHTY	MOTY
0	0.92(0.61)	0.92(0.61)	0.92(0.61)	0.92(0.61)	0.92(0.61)
0.05	1.39(0.95)	1.52(0.57)	2.48(1.55)	2.06(1.35)	2.30(0.70)
0.10	———	2.35(0.45)	3.04(1.34)	3.45(1.37)	3.28(0.66)
0.13	———	3.80(0.44)	3.63(1.29)	3.60(0.96)	3.44(1.00)
0.15	———	4.16(0.69)	3.84(1.66)	4.75(1.68)	3.51(0.83)
0.17	———	3.36(0.79)	3.46(1.22)	4.68(1.25)	3.46(0.92)
0.20	———	2.79(1.01)	2.85(0.78)	3.17(1.23)	3.28(1.57)

n=12～20, SD in parentheses
Means connected by bars were not significantly different.

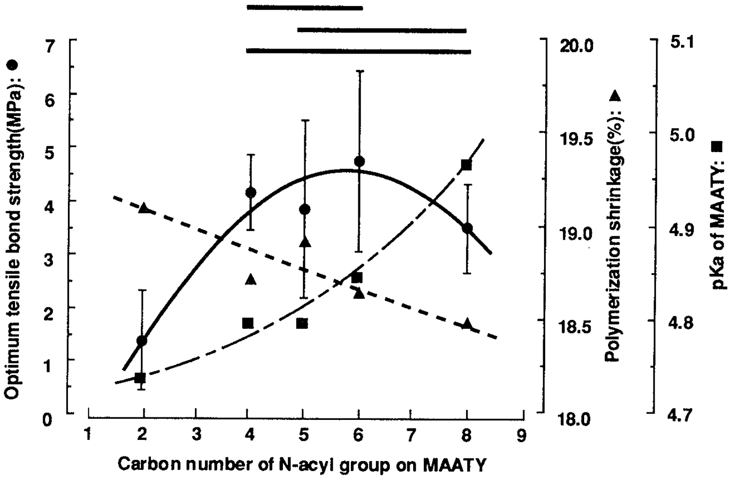

Fig. 2 Relationship between the adhesive strength, shrinkage at copolymerization, pKa of MAATY and the carbon number of the *N*-acyl group in MAATY. Means connected by bars were not significantly different on the bond strength.

carboxyl group on MAATY tended to increase tendency with increasing carbon atoms of the *N*-acyl chain.

DISCUSSION

The tensile bond strength of each MAATY-HEMA system to unetched human dentin (#600) was more sensitive to the monomer feed ratio than DMTY-HEMA system[4]. The former consisted of tyrosine and it was bifunctional with regard to the polymerizing factor, with HEMA as showing in Table 2. The optimal tensile bond strength on each MAATY-HEMA system was 15 mol% in the monomer feed of MAATY. This was similar to the optimum monomer feed composition in the majority of adhesive monomers, which continued monofunctional monomers for polymerization, which is in the neighborhood of 5～10 mol%.[6~8] On the other hand, the optimum tensile bond strength of copolymerization systems of a series of methacrylates, consisting of tyrosine with HEMA, was 30 mol% in the monomer feed of the methacrylates.[4,5]

There are four influences of the introduced acyl groups with various chain lengths, on the amino group in the neighborhood of the carboxyl group of tyrosine in MAATY, on the tensile bond strength of MAATY-HEMA and unetched human dentin. That is, increasing hydrophobicity, steric hindrance of the carboxyl group, affecting its pKa and decreasing the polymerization shrinkage. Thus the optimum tensile bond strength of MAATY-HEMA systems to unetched human dentin tended to become greater with increasing the carbon number of the *N*-acyl group. The MHTY (n=6)-HEMA system showed a peak, which was smaller in that of MOTY (n=8) with a longer acyl chain, as shown in Fig. 2. The hydrophobicity index of the *N*-acyl groups is represented by the carbon number, so it increased following the increase of the carbon number in the order: MATY<MBTY<MVTY<MHTY<MOTY. Therefore, the tendency of the optimum tensile bond strength of MAATY-HEMA bonding systems cannot be determined only from the hydrophobicity of *N*-acyl groups. The pKa of the carboxyl group on MAATY increases and polymerization shrinkage of MAATY-HEMA system decreases following an increase in the carbon number of the *N*-acyl group as shown in Fig. 2. The increasing pKa and decreasing polymerization shrinkage are convenient for adhesion to dentin. The tendency of an MAATY, except MOTY, can be determined by the pKa and polymerization shrinkage. However, MOTY-HEMA bonding system have low adhesive strength despite their favorable pKa and low polymerization shrinkage.

Kawaguchi *et al.*[9] calculated using Hydrophile-lipophile balance (HLB) numbers[10,11] the relationship among several monomers for evaluating the effect of the hydrophilic and hydrophobic group of the monomer with a carboxyl group as a functional group in the adhesive bonding to unetched dentin. The results indicated that the adhesive strength was highest when the HLB number of the adhesive monomer was near 7; that is, the hydrophobic and hydrophilic properties were equivalent. Thus, the HLB numbers of MAATY were calculated according to Griffin's equation[11], and the relationship between the optimum tensile bond strength of MAATY-HEMA systems and the HLB numbers of MAATY are shown in Fig. 3. MAATY, except for MOTY, functioned in the same manner as described by

Kawaguchi *et al.*[9]. The closer the HLB numbers of MAATY to 7, the higher the optimum tensile bond strength of MAATY-HEMA system. MOTY had low adhesive strength although its the HLB number is near 7.

These results suggest that there are several causes of the low adhesive strength of the MOTY-HEMA system. The increasing steric hindrance of the *N*-acyl groups following the increasing carbon numbers of *N*-acyl groups should be considered. Regarding bonding agents consisting of methacrylates containing tyrosine, *N, O*-dimethacryloxy tyrosine ethyl ester as an adhesive monomer scarcely adhered to the unetched tooth substance[5]. This shows that the adhesion of a bonding agent consisting of MAATY to the tooth substance, is mainly due to the hydrogen bond formed between the carboxyl group on MAATY and the tooth surface. As described above, increasing the carbon number of the *N*-acyl group means increasing the steric hindrance to the carboxyl group, which plays the leading role in adhesion between the adhesive monomer and the tooth substance. It is assumed that the steric hindrance of *N*-octanoyl group (n=8) contrasts in a striking way with that of *N*-hexanoyl group (n=6) to the carboxyl group. To confirm this assumption, molecular structures in space filling and wire frame molecular models of MAATY in which the steric hindrance of the *N*-acyl group (the red solid line in molecular model) to the carboxyl group (the blue solid line) is the largest, were assembled by a molecular modelling program+ (Fig. 4). *N*-Acyl groups of n=6 and below, namely, *N*-acetyl, *N*-butyryl, *N*-valeryl and *N*

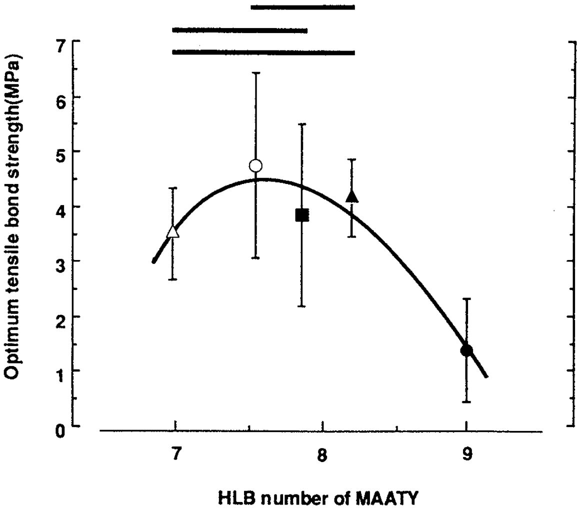

Fig. 3 The relationship between the HLB values of MAATY and the optimum tensile bond strength of MAATY-HEMA systems to the unetched human dentin. Means connected by bars were not significantly different.

●: MATY (5)-HEMA
▲: MBTY (15)-HEMA
■: MVTY (15)-HEMA
○: MHTY (15)-HEMA
△: MOTY (15)-HEMA

+ Chem 3 DPlus Ver. 3, Cambridge Scientific Computing, Inc., MA, USA

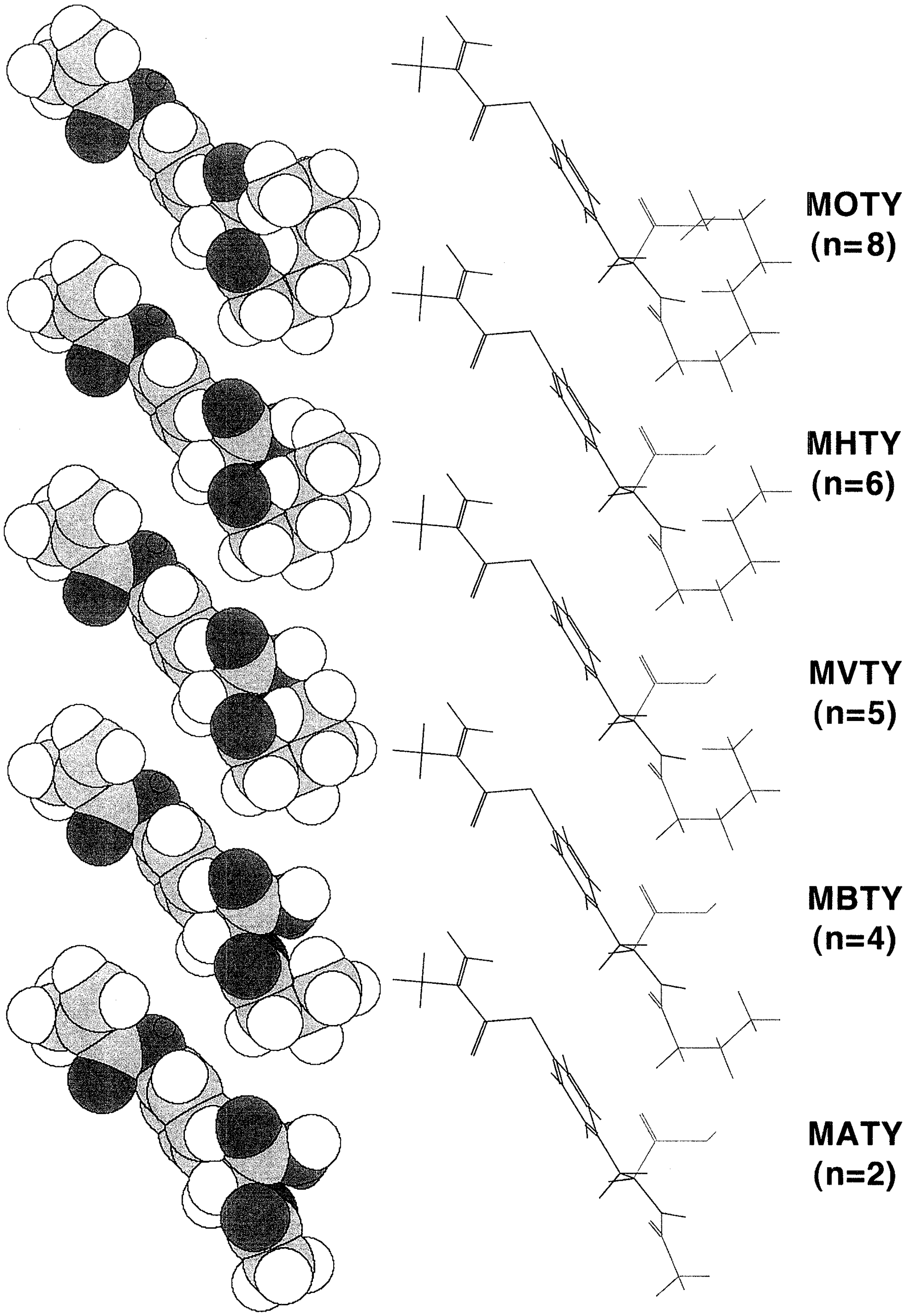

Fig. 4 A three-dimensional demonstration of the steric hindrance of the *N*-acyl group on MAATY to the carboxyl group.

-hexanoyl, cannot mask the carboxyl group due to their length. Nevertheless, the *N*-octanoyl group on MOTY can do so, as shown in Fig. 4. Only the *N*-octanoyl group is involved in the steric hindrance of the formation of a hydrogen bond between the carboxyl group on MAATY and tooth substance.

The maximum tensile bond strength to unetched human dentin was shown with a bonding system containing MHTY in a series of MAATY in this study. The tensile bond strength (4.75 MPa) of the MHTY (15 mol%)-HEMA bonding system was equal to or greater than that (4.31 MPa) of DMTY-HEMA, which has the maximum tensile bond strength among all methacrylates containing phenylalanine as a bone structure$^{12)}$.

CONCLUSION

The optimal molecular structure of a monomer with a carboxyl group for use as an adhesive to unetched dentin would be as follows.

1) A flexible carboxyl group on the MAATY,
2) Balanced hydrophobic and hydrophilic properties in the functional monomer,
3) No steric hindrance of the neighbor to the carboxyl group.

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2種の結晶を含有するキャスタブルガラスセラミックスの機械的強さに及ぼす結晶化の影響

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アパタイトとチタン酸マグネシウムの2種の結晶が析出するキャスタブルガラスセラミックスの機械的性質に及ぼす結晶化（セラミング）の影響を検討するため，結晶化処理温度を変化させ，曲げ強さ，破壊靱性および硬さなどを調べた．その結果，結晶化処理したガラスセラミックスの曲げ強さは結晶相の増加につれて高くなることがわかった．ガラスセラミックス中に析出するチタン酸マグネシウムは同量のアパタイトの析出に比較し，強さに対して効果的であることが示唆された．破壊靱性はアパタイト結晶だけを析出させた試験片で，アズキャストの場合に比較して，2倍の値が得られた．このことは硬さの低いアパタイト粒子でもクラックのピン止め効果を持つものと考えられた．本材料は市販のボディー用陶材より高い機械的性質が得られたことから，審美補綴材料として使用できる可能性が示唆された．

O-メタクリロイル-N-アシルチロシンの合成と無処理人歯象牙質に対する接着性

田仲持郎，鈴木一臣，中井宏之

岡山大学歯学部歯科理工学講座

接着性モノマーの分子構造と接着性との相関を調べることを目的として，種々の長さのアシル鎖を持つO-メタクリロイル-N-アシルチロシン（MAATY）を合成，それらを含むボンディング剤を調製し，その無処理人歯象牙質に対する接着強さについて検討した．その結果は，チロシン骨格のカルボキシル基の自由度の増大が歯質との相互作用にとって好ましく強固な接着の要因であると考えられた．又，立体障害，疎水性といったカルボキシル基近傍の構造，モノマー分子の疎水性—親水性のバランス，共重合系の重合収縮が重要であることが示唆された。特に，カルボキシル基の隣接基の立体障害がO-メタクリロイル-N-オクタノイルチロシンの場合には極めて重要であった。最大接着強さはO-メタクリロイル-N-ヘキサノイルチロシン（15 mol %）-HEMA（85 mol %）から成るボンディング剤で得られ，その接着強さ（4.75 MPa）はフェニルアラニンを骨格に持つメタクリレートのうちで最大であった．

リン酸で処理した象牙質への接着における銅イオン含有プライマーの効果

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象牙質界面での重合を促進することが可能な銅イオンを含むプライマーについて検討した．牛歯象牙質表面を10％リン酸水溶液で前処理した後，0.03％の銅塩を含む35％2-ヒドロキシエチルメタクリレート（HEMA）水溶液からなるプライマーを塗布し，4-META/MMA-TBBOレジンで接着した．このプライマーを用いることにより，プライマーを用いないときの接着強さ3.8 MPa，あるいは銅塩を含まない35％HEMAプライマ