

Synthesis of Polyester Pigment Binders Containing Dimethyl 2,2-Dimethyl-4-methylene Glutarate

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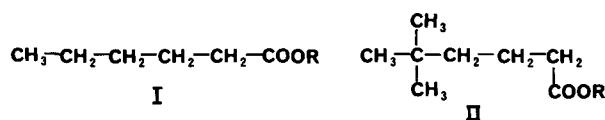
SYNOPSIS

Low molecular weight oligomers of dimethyl 2,2-dimethyl-4-methylene glutarate and neopentyl glycol have been synthesized. These oligomers were chain-extended with select diacids and diols to polyesters that were used as pigment binders in paint formulations. Such paints were shown to possess superior detergent resistance when compared to paints formulated using pigment binders that did not contain dimethyl 2,2-dimethyl-4-methylene glutarate.

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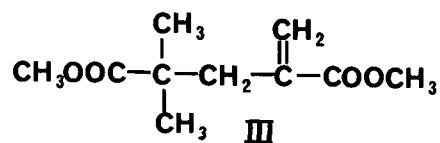
INTRODUCTION

Turpin¹ showed that increased branching near the ester linkage in a polyester results in increased hydrolytic stability and chemical resistance for that polyester. In addition, esters having an increased number of carbon atoms located at positions 5, 6, or 7 atoms away from the ester linkage show an improved hydrolytic stability and chemical resistance due to the ability of such groups to sterically shield the ester linkage via various cyclic structures, i.e., Newman's "Rule of Six."² For example, given the above, molecule I would be expected to be less resistant to hydrolysis than is molecule II due to the presence of additional methyl groups located 6 atoms from the ester linkage in molecule II:



Recently, we showed the feasibility of obtaining the methyl methacrylate dimer, dimethyl 2,2-dimethyl-4-methylene glutarate (DMDMMG), in

high yields via a metal-catalyzed chain transfer (MECCA) process.^{3,4} The dimer is an unsymmetrical aliphatic diester in which one of the ester moieties is a sterically hindered tertiary ester (Structure III)^{5,6}:



Incorporation of a unit such as III into a polyester would have the effect of increasing the hydrolytic stability and chemical resistance of the polyester, particularly if a hindered diol such as neopentyl glycol (NPG) is used as a comonomer.

The work that is reported herein was undertaken to evaluate the effect on hydrolysis resistance that incorporation of DMDMMG into a polyester pigment binder used in a high solids paint formulation would have.

EXPERIMENTAL

Materials

Dimethyl 2,2-dimethyl-4-methylene glutarate (DMDMMG) was synthesized as previously described^{3,4} and distilled before use. The transes-

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terification catalysts were reagent-grade materials obtained commercially and used as received. Neopentyl glycol (NPG), 1,6-hexanediol, isophthalic acid, trimethyloethane, and Cymel 1133 were all commercial-grade materials and were used as received. All solvents were commercial grade and were used without further purification.

Methods

NMR measurements were performed at ambient temperature on a Perkin-Elmer R-12B 60 MHz ¹H-NMR spectrometer operating in the CW mode. The samples were dissolved in CDCl₃, and TMS was added as an internal standard.

Molecular weight measurements were made using Varian Micropak TSK 2000H and 3000H columns for low molecular weight materials and a Waters 150 ALC/GPC equipped with 1 × 10⁶, 1 × 10⁵, 1 × 10⁴, 1 × 10³, 500, and 100A columns for higher molecular weight materials. Tetrahydrofuran at 50°C was used as the eluent in all cases. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Specular gloss (60° and 20°) was measured using a Hunterlab D48D glossmeter. Film thicknesses were measured with a Fischer Permascope ES.

Detergent resistance was tested in a chamber equipped with a detergent bath consisting of sodium carbonate, sodium *m*-silicate, sodium sulfate, a sodium alkyl-aryl sulfonate, and pyrophosphate totaling 444 g in 8 gal of distilled water. Test panels, prepared as detailed below, were soaked in this detergent bath at 73°C for a period of 10 days. The

panels were then removed from the bath, rinsed with distilled water, and air-dried and the paint performance analyzed.

General Method of Synthesis of DMDMMG–NPG Oligomers by Transesterification

The required amounts of NPG, DMDMMG, and catalyst were combined in a 500 mL four-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, short Vigreux column, Dean-Stark trap, and reflux condenser. The contents of the flask were heated under nitrogen to 110–130°C and held in this temperature range while approximately 50% of the calculated amount of methanol was collected. The temperature of the reaction mixture was then gradually raised (~ 1°C/min) to 180–200°C and an additional quantity of methanol was collected. Heating at 180–200°C was continued until no further methanol was collected in the Dean-Stark trap for a period of 0.5 h. The cooled product, a pastelike solid in all cases, was characterized by NMR spectroscopy and GPC.

Synthesis of Polyester Binder Containing DMDMMG–NPG Oligomer

A typical binder synthesis was performed as follows: A 3L four-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, reflux condenser, and Dean-Stark trap was charged with NPG (336.0 g, 3.23 mol), DMDMMG–NPG oligoester $M_w = 770$ (677.0 g), isophthalic acid (831.0 g, 5.00 mol), trimethyloethane (124.0 g, 1.03 mol),

Table I Synthesis of DMDMMG–NPG Oligomers

Sample No.	NPG (Mol)	DMDMMG (Mol)	Catalyst	Catalyst Concentration (Wt %)	Reaction Temperature (°C)	Reaction Time (h)	% Reaction ^a	\bar{M}_w	\bar{M}_w/\bar{M}_n
1	1.50	1.50	LiCO ₃	0.5	120–220	4.0	0	—	—
2	0.75	0.25	TIPT ^b	0.3	120–220	3.5	0	—	—
3	1.50	0.50	NaOCH ₃	1.0	110–195	3.5	100	980	1.87
4	1.50	0.50	Co(AcAc) ^c	1.0	120–200	3.0	10	321	1.20
5	1.50	0.50	NaOCH ₃ / 18-Crown-6	0.5/2.4	150–190	1.0	100	763	1.60
6	1.50	0.50	LiOH	0.5	110–180	6.5	96	774	1.55
7	1.50	0.50	KOH	0.5	130–190	1.5	95	624	1.49
8	2.00	0.67	NaOC(CH ₃) ₃	0.5	130–200	2.3	96	770	1.58
9	1.50	0.50	NaOC ₂ H ₅	0.5	130–200	2.0	71	—	—

^a Measured by amount of methanol collected.

^b Tetraisopropyl Titanate (DuPont "Tyzor").

^c Cobalt acetyl acetate.

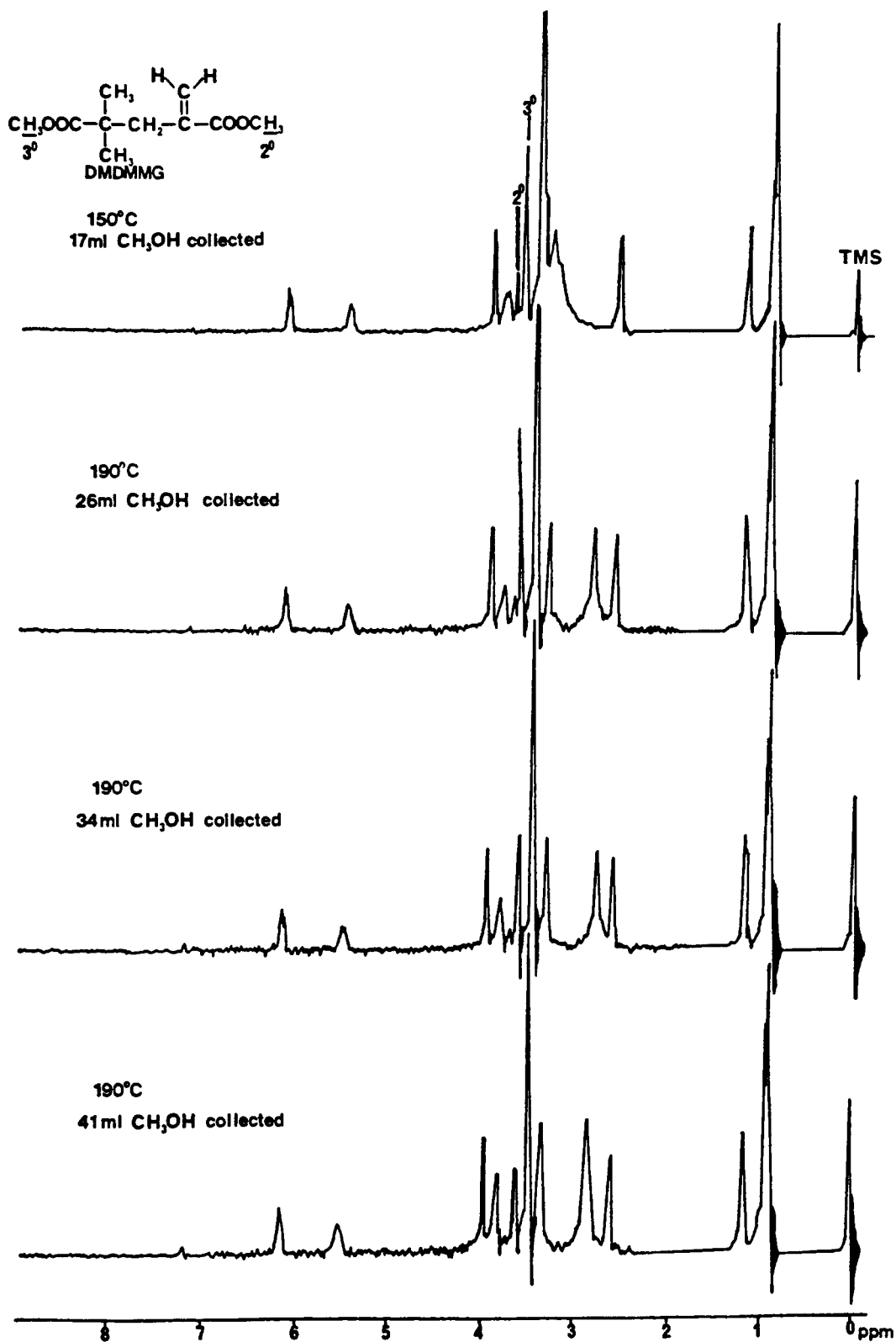


Figure 1 $^1\text{H-NMR}$ spectra of the reaction product of NPG and DMDMMG catalyzed by KOH.

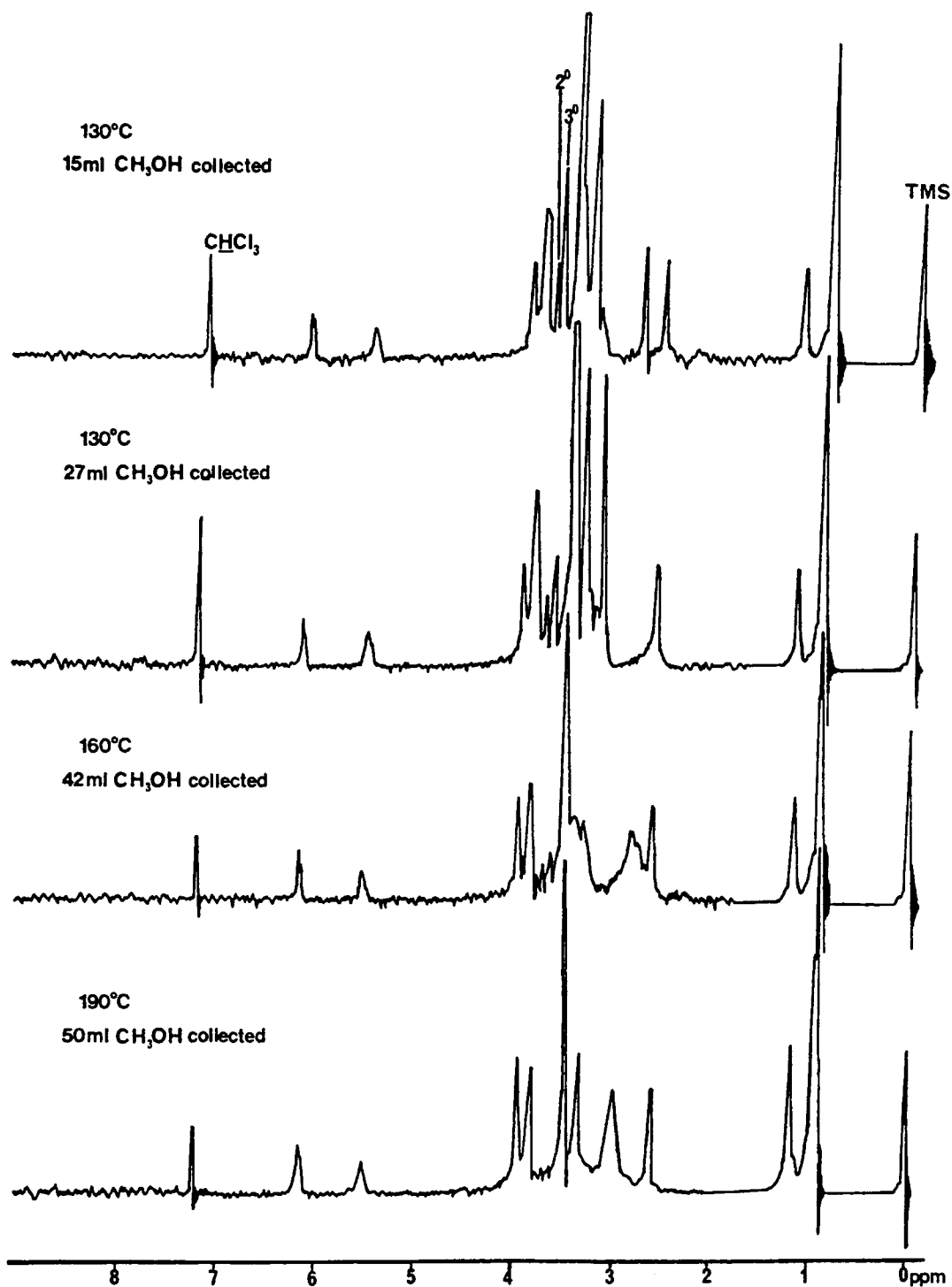


Figure 2 $^1\text{H-NMR}$ spectra of the reaction product of NPG and DMDMMG catalyzed by NaOCH_3 .

and butyl stannic acid (9.84 g, 0.047 mol). The reaction mixture was heated under nitrogen with stirring to 130°C , at which point evolved water began to collect in the Dean-Stark trap. The reaction tem-

perature was gradually increased to 180°C over a period of 3 h, at which time the amount of evolved water collected indicated that the reaction was 98% complete. The branched polyester thus obtained

Table II Composition of Polyester Binders

Sample	DMDMMG ^a (Wt %)	NPG ^b (Wt %)	1,6-Hexanediol (Wt %)	Isophthalic Acid (Wt %)	Trimethylolethane (Wt %)
Control	0.0	23.4	17.7	49.7	9.2
A	5.6	23.5	17.8	43.8	9.3
B	16.0	20.9	10.3	44.5	8.3
C	24.0	19.8	6.5	41.8	7.8
D	16.4	41.9	0.0	39.3	6.3
E	24.5	27.0	0.0	42.2	2.4

^a Calculated from wt % DMDMMG contained in DMDMMG-NPG prepolymers.

^b Total amount of NPG including that contained in DMDMMG-NPG prepolymers.

has a hydroxyl number of 142 and an acid number of 6.8.

Although the synthesis given above is an example of a typical binder synthesis, it should be noted that in some of the polyester binders examined in this study 1,6-hexanediol was used as a component, replacing a portion of the NPG and/or the isophthalic acid.

Typical molecular weights for the polyesters binders obtained as detailed above ranged from $M_w = 1600$ to $M_w = 2600$ with polydispersities from 1.60 to 1.96.

Synthesis of Control Polyester Binders

These polyesters were synthesized in the same manner as those above, with the exceptions that they (the controls) contained no DMDMMG and were synthesized in a single stage without the preparation of a prepolymer. The acid and hydroxyl numbers as well as the molecular weights obtained fell in the same range as the DMDMMG-containing polyester binders.

Formulation of High Solids Paints

The high solids paints evaluated in this study were formulated by mixing 50 parts of one of the polyester resins obtained above (as a 79 wt % solution in PM-acetate) with 20 parts acrylic pigment grind and 30 parts Cymel 1133 cross-linker.

The acrylic pigment grind was composed of 25 parts acrylic resin, 6.67 parts carboxylated acrylic resin, 0.1 parts leveling agent, 2.42 parts butyl carbitol, 2 parts *n*-butanol, 90 parts rutile titanium dioxide, and 4 parts methyl isobutyl ketone.

The formulated paints were sprayed to a thickness of 1.8 mil onto Parker B-1000 iron phosphate cold-rolled steel panels that had been primed with

1.2 mil of Pittsburgh Plate Glass (PPG) white primer. The panels were then baked at 180°C for 20 min to effect cure and, after cooling, were tested for detergent and salt spray resistance.

RESULTS AND DISCUSSION

The results obtained in the DMDMMG-NPG oligoester synthesis (Table I) strongly indicate that the most effective oligomerization catalysts, from the standpoints of conversion and molecular weight, are the alkali metal hydroxides and alkoxides. The transition metal and alkali metal carbonate catalysts are either much less effective or totally ineffective in bringing about a condensation reaction between DMDMMG and NPG.

The asymmetric nature of the DMDMMG molecule provides two methoxylate termini with different degrees of steric congestion that show discrete reactivities when the appropriate catalysts are used.

Table III Some Properties of the Pigmented High Solids Paints after a 180°C 20 Min Bake

Sample	Gloss ^a		Impact Resistance (in lb)		Conical Mandrel (in.)
	60°	20°	Forward	Reverse	
Control	96	69	30	3	1 $\frac{5}{8}$
A	97	71	32	2	1 $\frac{1}{4}$
B	95	68	30	2	2
C	94	67	34	2	1 $\frac{3}{8}$
D	91	69	30	1	2
E	85	58	32	3	1

^a The gloss is measured at the 60° and 20° angles of incident light and expressed as a percentage of light reflected, all the light reflected being the highest rating.

Table IV Salt Spray and Detergent Resistance of DMDMMG-containing Polyester Binders

Sample	Time of Exposure		Blister Size ^a		Blister Density ^b	
	Salt Spray	Detergent Bath	Salt Spray	Detergent	Salt Spray	Detergent ^c
	(h)	(Days)				
Control	500	10	5	8	10	F
A	500	10	7	9	5	VF
B	500	10	6	9	3	VF
C	500	10	6	8	2	VF
D	500	10	6	9	2	VVF
E	500	10	7	8	9	VF

^a Blister size designation according to ASTM D714 Test Method where size is represented on a numerical scale of 10 to 0 with 10 representing no blistering and lower numbers representing progressively larger blister sizes.

^b Blister density refers to the number of blisters per 24 in² test panel.

^c F = few, VF = very few and VVF = very, very few (ASTM D714).

At temperatures between 100 and 130°C, transesterification occurs primarily on the secondary methoxylate group of DMDMMG with the tertiary methoxylate group of DMDMMG reacting between 170 and 200°C. Figures 1 and 2 show ¹H-NMR spectra of reaction products as a function of reaction temperature and amount of methanol collected. The spectra in Figure 1 are of the product obtained from a reaction between 0.5 mol of DMDMMG and 1.5 mol of NPG in which potassium hydroxide was used as a catalyst. This catalyst showed a definite selectivity toward the secondary methoxylate moiety of DMDMMG as measured by the relative intensities of the resonances at $\delta = 3.60$ ppm and $\delta = 3.68$ ppm, which are assigned as shown in the figure.⁶ Even after reaching the maximum reaction temperature of 190°C and collecting a nearly theoretical amount of methanol, a portion of the tertiary methoxylate groups remain unreacted. The spectra in Figure 2 were obtained on products of a reaction between 0.5 mol of DMDMMG and 1.5 mol of NPG where sodium methoxide was used as a catalyst. Clearly, after the maximum reaction temperature of 195°C is reached and the theoretical amount of methanol collected, very little, if any, of either methoxylate group of DMDMMG remains unreacted. The difference in effectiveness between the potassium hydroxide and sodium methoxide catalysts can most probably be explained in terms of the differences in the base strengths and compatibilities with the reaction medium of the two catalysts.^{1,4}

As previously described, the DMDMMG-NPG oligoesters obtained were formulated into polyester binders, the compositions of which are summarized in Table II.

Some of the physical properties of the cured high solids paints formulated using the polyester binders

listed in Table II are summarized in Table III. The data presented in Table III shows that as the weight percent of DMDMMG is increased no loss of gloss is suffered in the paint films, but, in most cases, as shown by reverse impact resistance tests and a flexibility test (Conical Mandrel bend test; numbers are the inches from the cone tip that the cracking begins; the smaller the number the more flexible the film), some flexibility is lost as more 1,6-hexanediol is replaced with DMDMMG. The exception is Sample E, which retains the flexibility of the control; however, this is most probably because significantly less trimethylethane was used in the polymer synthesis, thus providing fewer cross-linking sites and reducing cross-link density. Other tests (not shown in Table III) confirmed that the DMDMMG-containing materials had equal solvent resistance (as measured by resistance to maring when the painted panels were rubbed with methyl ethyl ketone) and equal color quality and hardness (pencil) as compared to the control material.

The results from the salt spray and detergent resistance tests (Table IV) show that as the amount of DMDMMG is increased from 6 to 25 wt % detergent and salt spray resistance, as measured by blister size and density (ASTM D714), generally improved. Much better performance is obtained when both the levels of DMDMMG and NPG are high and no 1,6-hexanediol is present, as in Sample D, although Sample B, which contains 10.3 wt % 1,6-hexanediol, also has good performance, most probably due to a higher cross-link density, as Sample B contains more trimethylethane than do Samples C, D, and E. Sample B performs better than does Sample A because it (Sample B) contains significantly less 1,6-hexanediol. These results indicate that incorporation of branched species such as

DMDMMG-NPG oligomers into polyesters have the desired effect of increasing the hydrolytic stability of the polyester. The size of the blisters formed in both the salt spray and detergent resistance tests was not significantly reduced for the DMDMMG-containing materials vs. the control materials; however, the number of such blisters was significantly reduced.

CONCLUSIONS

The synthesis of oligomers containing a dimer of methyl methacrylate, dimethyl 2,2-dimethyl-4-methylene glutarate, and neopentyl glycol has been accomplished. Alkali metal hydroxides and alkoxides were found to be most effective catalysts for this oligomerization. Incorporation of these oligomers into polyesters used as pigment binders in high solids paints was found to improve the detergent and salt

spray resistance of such paints while maintaining other important paint properties such as gloss, color, solvent resistance, and hardness, at desired levels.

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