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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Hergenrother, P. M.(1973) 'Polyastriazines from Oxalamidrazone', Journal of Macromolecular Science, Part A, 7: 3, 573 — 585

To link to this Article: DOI: 10.1080/00222337308061159

URL: <http://dx.doi.org/10.1080/00222337308061159>

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Poly-as-triazines from Oxalamidrazone*

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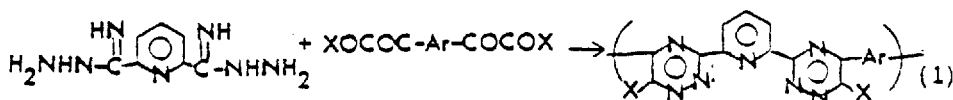
ABSTRACT

High molecular weight soluble poly-as-triazines were prepared by solution cyclopolycondensation of oxalamidrazone with various bisglyoxals and bisbenzils. Solutions of the phenyl-substituted poly-as-triazines at solids content of ~20% are metastable, increasing in viscosity and, in some cases, gelling. The gelling phenomenon can be alleviated without any appreciable detrimental effect upon the polymer by upsetting the stoichiometry of the reactants. Relatively high molecular weight polymer (e.g., $\eta_{inh} = 1.76$) can be obtained when the stoichiometry is upset by 1% in favor of either reactant. Polyphenyl-as-triazines films exhibited room temperature (RT) tensile strength as high as 16,400 psi (tensile modulus of 400,000 psi and ultimate elongation of 5%). Titanium and stainless steel tensile shear specimens provided RT strength of 2850 and 3400 psi, respectively. Polyphenyl-as-triazines exhibit good thermal oxidative stability after aging for 1000 hr at 500° F (260° C) in circulating air.

*Presented in part at the 164th National Meeting of the American Chemical Society, New York, New York, August 1972.

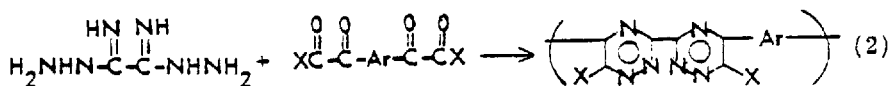
INTRODUCTION

The preparation of high molecular weight soluble poly-as-triazines by the cyclopolycondensation of 2,6-pyridinediyl diamidrazone (dihydrazidine) with an aromatic bisglyoxal and with various aromatic dibenzils, as shown in Eq. (1), have been reported [1, 2]:



where X = H or C₆H₅, and Ar = arylene.

The work reported herein concerns the preparation of a variety of as-triazine polymers from the reaction of oxalamidrazone with various aromatic bisglyoxals and bisbenzils:



where X = H or C₆H₅, and Ar = arylene.

This work was performed primarily to determine the effect two as-triazine rings adjacent to each other in the backbone of the polymer chain has upon the overall properties of the polymer and to determine if these polymers exhibited any unique properties as structural or functional resins.

EXPERIMENTAL

Reactants

Cyanogen was prepared following a known procedure [3] from the reaction of potassium cyanide and copper sulfate.

Oxalamidrazone was prepared following a procedure by Dedichen [4]. Dicyanogen (16 g, 0.5 mole) was bubbled through a solution of hydrazine (95%, 120 ml) in ethanol (600 ml) at -10°C with vigorous stirring during 15 min. After complete dicyanogen addition the resulting white suspension was stirred for 1 hr at -10°C and filtered. The white solid was washed with cold ethanol and dried over phosphorus pentoxide in vacuo to yield a white crystalline solid (27 g, 46.5% yield), mp 179-180°C (dec, introduced into preheated oil bath at 160°C). Analysis: Calculated

for $C_2H_5N_6$: C, 20.68%; H, 6.94%; N, 72.37%. Found: C, 20.44%; H, 6.96%; N, 72.51%.

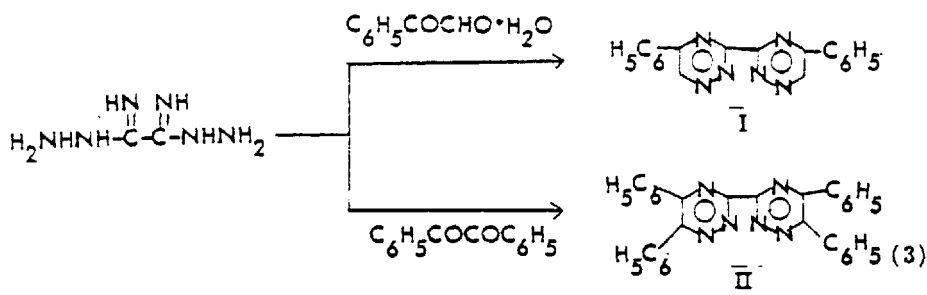
The aromatic bisglyoxals as reported in Table 1 were prepared following a known procedure [5] by the selenium dioxide oxidation of the aromatic diacetyl compounds (obtained by the Friedel-Crafts acetylation of the arylene compounds).

Para and meta-bis(phenylglyoxalyl)benzene were prepared as previously described [2].

The other dibenzil-type reactants as reported in Table 1 were prepared through a known procedure [1] by the selenium dioxide oxidation of the respective di(phenylacetyl) compound (obtained from the reaction of the arylene compound with phenylacetyl chloride and aluminum chloride).

Model Compounds

Two model compounds (I and II) as shown in Eq. (3) were prepared in essentially quantitative yields from the reaction of stoichiometric quantities of oxalamidrazone with phenylglyoxal hydrate and with benzil in refluxing ethanol. Model Compound I was obtained as a yellow solid (96% yield), mp 247-249°C, and recrystallized from a



1:1 mixture of N,N-dimethylformamide (DMF) and methanol to afford yellow needles, mp 249-250°C (lit. [14], mp 244-246). Model Compound II was obtained similarly as a yellow solid (97% yield), mp 298-300°C, and recrystallized from DMF (4 g/250 ml) to afford yellow needles, mp 301.5-302°C (lit. [4], mp 297°C).

Polymers

The unsubstituted poly-as-triazines (Polymers No. IP to III P, Table 2) were prepared by adding the bisglyoxal as a fine powder to a slurry of oxalamidrazone in m-cresol at 20% solids content. The

TABLE I. Characterization of Tetracarbonyl Compounds

| XOCOC-AR-COCOX | | Elemental analysis ^a | | | | |
|----------------------|-------------------------------|---------------------------------|---|--|------------------|----------------|
| Ar | X | Mp (°C) | Lit. mp (°C) | Formula | C (%) | H (%) |
| p-Phenylene | H ^b | 160-162(d.) | 110-111 [6] (140-150) [7] (162-164 [8]) | C ₁₀ H ₁₀ O ₆ | 53.18 (53.10) | 4.41 (4.46) |
| p,p'-Oxydiphenylene | H ^b | 141-143(d.) | 122 [5] (118-120 dec) [9] | C ₁₆ H ₁₄ O ₇ | 60.27 (60.36) | 4.39 (4.43) |
| p,p'-Thiodiphenylene | H ^b | 129-130(d.) | 100-100.5 [10] | C ₁₆ H ₁₄ O ₆ S | 57.35 (57.47) | 4.18 (4.22) |
| m-Phenylene | C ₆ H ₆ | 99-100 | 98-99.5 [11] | C ₂₂ H ₁₄ O ₄ | - | - |
| p-Phenylene | C ₆ H ₆ | 125-126 | 125-126 [12] | C ₂₂ H ₁₄ O ₄ | - | - |
| p,p'-Oxydiphenylene | C ₆ H ₆ | 105.5-106.5 | 106.4-107 [13] | C ₂₈ H ₁₈ O ₆ | - | - |
| p,p'-Thiodiphenylene | C ₆ H ₆ | 91.5-92.5 | 90-91.6 [13] | C ₂₈ H ₁₈ O ₅ S | - | - |

^aTheoretical values in parenthesis.^bAs the dihydrate.

reaction mixture was heated to 70°C for 2 hr to form a viscous yellowish-orange solution (except for Polymer IP). The resulting viscous solution was poured slowly into methanol in a Waring Blender to precipitate a fibrous yellow solid which was thoroughly washed in hot methanol. After drying for 4 hr at 130°C in vacuo, the yellow polymer was characterized as shown in Table 2. Polymer IP was also prepared following this procedure, but failed to form a complete solution even at 5% solids content.

The phenyl-substituted poly-as-triazines (Polymers No. IVP to VIIP, Table 2) were prepared at 10% solids content in *m*-cresol, 1:1 mixture of *m*-cresol and xylene, chloroform, or sym-tetrachloroethane by adding the tetracarbonyl reactant to a slurry of oxalamidrazone. After stirring at ambient temperature for 1 hr a viscous solution formed which was stirred overnight. Polymer isolation and drying were performed as previously described for the unsubstituted polymers. Characterization is given in Table 2.

Discussion

Prior to polymer synthesis, two model compounds, as shown in Eq. (3), were prepared to serve as a guide for polymer synthesis and identification. The two model compounds were obtained in essentially quantitative yield as relatively pure materials.

As shown in Eq. (2) and Table 2, several as-triazine polymers were prepared from the reaction of oxalamidrazone with various bisglyoxals and bisbenzils. The unsubstituted as-triazine polymers were generally prepared as the soluble high molecular weight form in *m*-cresol at 20% solids content at temperatures of ~70°C except for Polymer No. IP. During the preparation of this polymer in *m*-cresol the polymer precipitated from solution as an orange solid. Even at 5% solids content, Polymer IP failed to dissolve completely in *m*-cresol or in several other solvents such as hexamethylphosphoramide (HMPA) and dimethyl sulfoxide (DMSO). The other two unsubstituted as-triazine polymers (IIP and IIP) readily formed viscous solutions at 20% solids content in *m*-cresol, but failed to form complete solutions in HMPA or DMSO at 5% solids content.

The polyphenyl-as-triazines (IVP to VIIP) were prepared in high molecular weight form from the reaction of oxalamidrazone with various bisbenzils in solvents such as *m*-cresol, 1:1 mixture of *m*-cresol and xylene, chloroform, or sym-tetrachloroethane at ambient temperature at solids content of 10%. A clear yellowish-orange viscous solution formed on a 0.010-M scale after ~0.5 hr, the time depending upon the reactivity of the dibenzil. Tough, flexible transparent yellow films were cast from these solutions.

TABLE 2. Characterization of Poly-as-triazines

| Ar | Structure, Eq. (2) | X | Polymer No. | η_{inh}^a | T_g^b ($^{\circ}C$) | Formula | Elemental analysis ^c | | |
|----|----------------------|----------|-------------|----------------|-------------------------|--------------------|---------------------------------|----------------|------------------|
| | | | | | | | C (%) | H (%) | N (%) |
| | p-Phenylene | H | IP | 0.65 | 260 | $C_{10}H_4N_6$ | 61.42 (61.53) | 2.51 (2.58) | 35.76 (35.89) |
| | p,p'-Oxydiphenylene | H | IIP | 1.48 | 244 | $C_{18}H_{10}N_6O$ | 66.19 (66.25) | 3.05 (3.09) | 25.64 (25.76) |
| | p,p'-Thiodiphenylene | H | IIP | 1.52 | 240 | $C_{18}H_{10}N_6S$ | 63.07 (63.14) | 2.89 (2.94) | 24.43 (24.55) |
| | m-Phenylene | C_6H_6 | IVP | 1.47 | 295 | $C_{24}H_{14}N_6$ | 74.15 (74.21) | 4.06 (4.15) | 21.49 (21.64) |
| | p-Phenylene | C_6H_6 | VP | 1.32 | 302 | $C_{24}H_{14}N_6$ | 74.11 (74.21) | 4.08 (4.15) | 21.53 (21.64) |
| | p,p'-Oxydiphenylene | C_6H_6 | VIP | 1.96 | 270 | $C_{30}H_{20}N_6O$ | 74.82 (74.99) | 4.07 (4.20) | 17.37 (17.46) |
| | p,p'-Thiodiphenylene | C_6H_6 | VIP | 1.85 | 260 | $C_{30}H_{20}N_6S$ | 72.48 (72.56) | 4.01 (4.06) | 16.81 (16.93) |

^a m-Cresol solution (0.5%) at 25°C.^b Glass transition temperatures (T_g) determined by differential scanning calorimetry at $T = 20^{\circ}C$ / min in N_2 .^c Theoretical values in parenthesis.

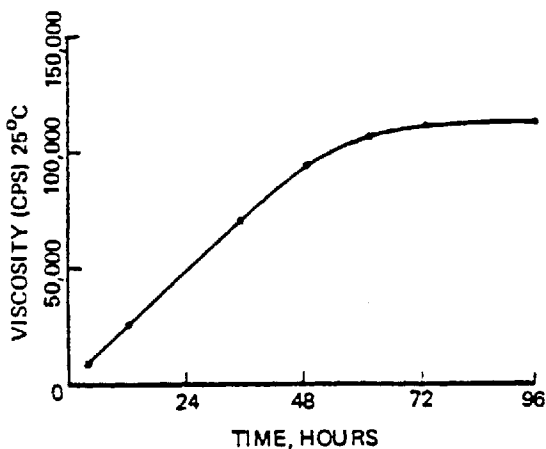
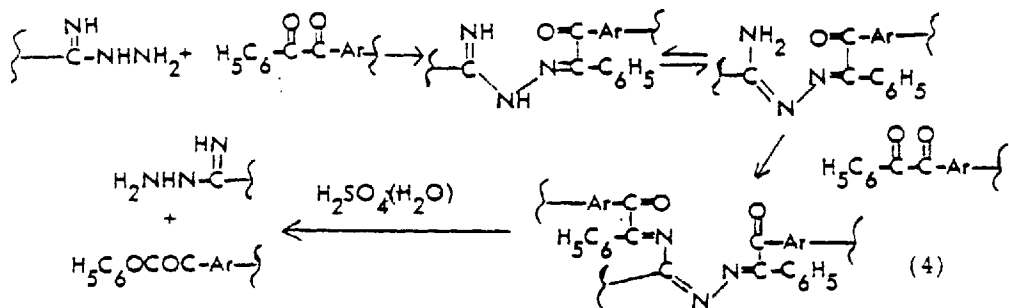


FIG. 1. Solution viscosity of a polyphenyl-as-triazine (VI) (20% solids content, 1:1 mixture of *m*-cresol and xylene).

At solids content of 20%, solutions of the phenyl-as-triazine polymers from stoichiometric amounts of high purity reactants are generally metastable, increasing in viscosity (Fig. 1) and in many cases exhibiting various degrees of gelation after stirring for 1 to 5 days. The gel, once formed, is irreversible. The polymer can be isolated from the gelled state by dilution with methanol and redissolved at a lower solids content (e.g., 5% instead of 20%). The gelling phenomenon is tentatively attributed to a combination of two factors, high molecular weight species and a small amount of branching. Evidence to support branching in some cases is based upon the fact that the inherent viscosity in concentrated sulfuric acid decreases gradually to a certain value and remains constant. The acid apparently hydrolyzes the cross-linked sites which are presumably Schiff bases as shown in Eq. (4). The assumption



is made that complete ring closure has occurred where possible; otherwise the incompletely ring-closed material would also undergo cleavage, resulting in a decrease in the dilute solution viscosity. For example, as shown in Fig. 2 for a polymer having the structure of VIP

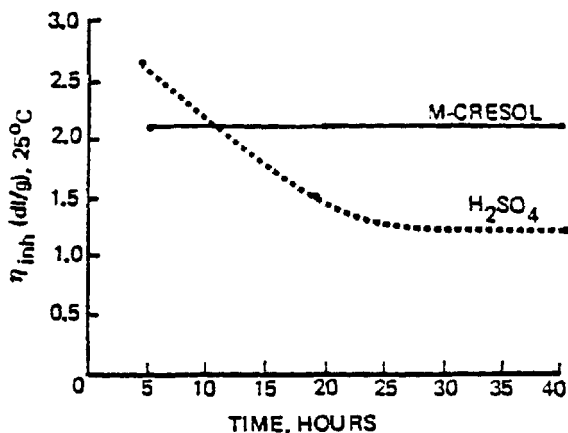


FIG. 2. Dilute solution viscosity of a polyphenyl-as-triazine(VI) (0.5% concentration at 25°C).

(Table 2), the inherent viscosity (η_{inh} , 0.5% concentration at 25°C) in concentrated sulfuric acid was initially 2.6 (as soon as solution formed) and decreased to 1.25 after an additional 20 hr, whereas the η_{inh} in m-cresol remain unchanged after 40 hr. The branching is assumed to be slight, since certain properties such as the glass transition temperature (T_g), as measured by differential scanning calorimetry (DSC), and the IR spectrum showed essentially no difference when compared with that of another sample of polymer of comparable molecular weight [$\eta_{inh} = 1.41$ (0.5% H_2SO_4 at 25°C), this one did not exhibit a decrease in the η_{inh} in H_2SO_4].

In addition, polymer isolated from other gelled solutions (20% solids content) exhibited no decrease in their dilute solution viscosity in sulfuric acid. Prior to gelling, half of the polymer solution was diluted to 10% solids content. This dilute solution did not gel. Hence, gelling here was tentatively attributed to high molecular weight forms ($\eta_{inh} = 2.4$) and the associated factors (association, entanglement, etc.).

In an attempt to alleviate the gelling problem, a brief study was

conducted on the synthetic procedure for polyphenyl-as-triazines. The general method of synthesis involved the addition of the tetracarbonyl reactant as a fine powder during about 5 min to a slurry of oxalamidrazone. Other modes of addition were also studied where the tetracarbonyl reactant as a powder was added over a relatively long period of time (e.g., 2.5 hr, 98% added during 0.5 hr, and remaining 2% added during 2 hr) and also where a solution (m-cresol) of the tetracarbonyl reactant was added during a period of 2 hr. In general, the mode of addition failed to have any significant effect upon alleviating the gelling problem at 20% solids content.

The gelling phenomenon can be overcome by upsetting the stoichiometry in polymer preparation. The effect of stoichiometric imbalance upon the properties of a polyphenyl-as-triazine is presented in Table 3. When the stoichiometry was upset by 1% in favor of the amidrazone or benzil reactant, relatively high molecular weight polymers ($\eta_{inh} = 1.61$ and 1.76) were obtained whose films provided high tensile strength (14,100 and 14,900 psi). Even when the stoichiometry was upset by 2.5%,

TABLE 3. Effect of Stoichiometry on PPT from the Reaction of Oxalamidrazone and p,p'-Oxydibenzil (20% solids content in 1:1 mixture of m-cresol and xylene, 0.02 mole scale)

| Mole of amidrazone/ 1.000 mole benzil | Solution viscosity (cP) ^a | η_{inh} (dl/g) ^b | Film (tensile strength, psi) |
|--|---|----------------------------------|---------------------------------|
| 0.975 | 24,000 | 1.07 | 6,700 |
| 0.985 | 35,000 | 1.23 | 8,300 |
| 0.990 | 78,000 | 1.61 | 14,100 |
| 0.995 | 87,300 | 1.92 | 16,900 |
| 1.000 | 115,000 | 2.31 | 17,400 |
| 1.005 | 84,000 | 1.87 | 16,400 |
| 1.010 | 80,600 | 1.76 | 14,900 |
| 1.015 | 52,000 | 1.44 | 9,200 |
| 1.025 | 35,500 | 1.25 | 7,000 |

^a Brookfield viscosity at 25°C.

^b m-Cresol solution (0.5%) at 25°C.

film-forming polymers with η_{inh} of 1.07 and 1.26 were obtained. This was unexpected since in condensation polymers formed from AA-BB

type reactants, stoichiometric quantities of reactants are generally required to form high molecular weight polymer (excluding interfacial condensation). This polycondensation exhibits many features of interfacial polycondensation and, as explained by Morgan [15], the rate of polymerization is faster than the rate of mixing or dissolution such that there may be temporary interfaces within which polycondensation is proceeding independently of the stoichiometry of the two reactants in the complete system.

Thermal Stability

The T_g s of the polymers as presented in Table 2 were determined by DSC at a heating rate of $20^\circ\text{C}/\text{min}$ in nitrogen. A typical curve is shown in Fig. 3.

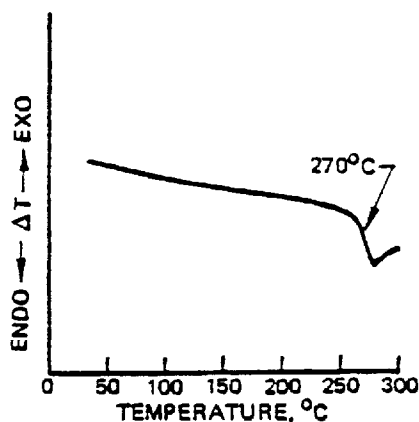


FIG. 3. Differential scanning calorimetry of a polyphenyl-as-triazine (VI) ($\Delta T = 20^\circ\text{C}/\text{min}$, N_2).

The thermal stability of the polymers was determined by thermogravimetric analysis (TGA). A typical thermogram is shown in Fig. 4. As previously shown [1, 2], as-triazine polymers undergo a 2-stage decomposition in both air and nitrogen. A thermal degradation study [16] on as-triazine polymers showed that initial degradation occurred in the as-triazine ring by thermal cleavage of the N-N bond. As-triazines polymers reported in this paper, where two as-triazine rings are adjacent, are less thermally stable than the as-triazine

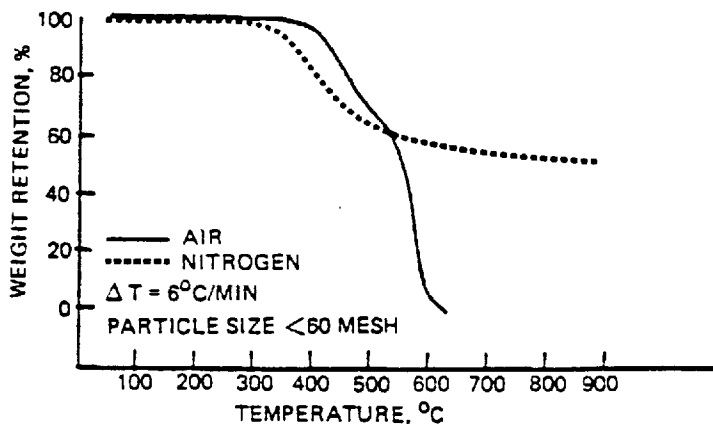


FIG. 4. Thermogravimetric analysis of a polyphenyl-as-triazine (VI).




polymer previously reported [1, 2] where the as-triazine rings were separated by a pyridine moiety (2,6-position).

The thermaloxidative stability of the polymers was determined by isothermal aging on films at 450° F (232° C) and at 500° F (260° C) in circulating air. The films were prepared by doctoring the polymer solution (10% solids content) in a mixture (1:1) of m-cresol and xylene onto plate glass followed by drying in a forced air oven at ~70° C for 8 hr. After further drying at 130° C for 4 hr in vacuo the transparent yellow films exhibited the aging properties as presented in Table 4. The phenyl-substituted as-triazine polymers exhibited excellent oxidative stability at 232 and 260° C in air for 1000 hr whereas the unsubstituted poly-as-triazine underwent pronounced degradation after 450 hr at 232° C.

Mechanical Properties

Polymer IVP (Table 2) underwent preliminary evaluation as an adhesive. No optimization of process parameters such as surface preparation, primer, filler, tape weight, or cure conditions was performed. Standard tensile shear specimens were fabricated under process conditions derived from preliminary flow tests on the adhesive tape. An unfilled tape (9 mils thick, ~4% volatile content) was prepared by solution coating 112-E glass with A-1100 finish followed by drying at 150° C in a forced air oven. Additional drying was done at 130° C in vacuo. Titanium (6Al-4V) and stainless steel (17-7PH) panels having a phosphate fluoride surface treatment were press cured, starting at room temperature and increasing the temperature

TABLE 4. Isothermal Aging of Poly-as-triazines

| Polymer structure | η_{inh}^a (dl/g) | Film thickness (mil) | Wt loss ^b after time (hr) in air at | | | | | |
|---|--------------------------|----------------------------|--|------|------------------|-------------|-------------------|------|
| | | | 20 | 454 | 1050 | 20 486 1030 | | |
|  | 1.48 | 1.8 | 5.4 | 69.5 | 72.2 | 8.3 | 50.6 | 72.4 |
|  | 1.96 | 2.0 | 6.8 | 8.3 | 9.5 ^c | 6.9 | 17.6 ^d | 28.1 |
|  | 1.88 | 2.4 | 4.2 | 5.0 | 6.0 ^c | 4.4 | 9.4 | 15.7 |

^a 0.5% m-cresol solution at 25°C.

^b Circulating air.

^c Fingernail creasable.

^d Failed fingernail crease test at >300 < 371 hr.

to 525° F during ~0.5 hr and maintaining at 525° F for 1 hr under 100 psi. Titanium and stainless steel tensile shear specimens provided average room temperature strength of 2850 and 3400 psi, respectively. All failures were adhesive types and no testing was performed at elevated temperature.

Films of a poly-as-triazine (Polymer IVP, Table 2) prepared as previously described in the thermal stability section but further dried at 150° F in vacuo for 18 hr provided room temperature tensile strength as high as 18,400 psi, tensile modulus of 400,000 psi, and ultimate elongation of 5%.

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