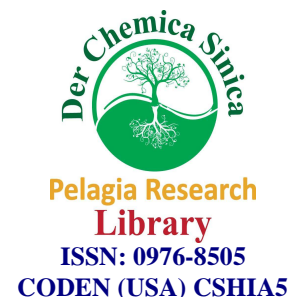




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Structural and Thermokinetic study of polyamide derived from 2, 6 -diaminopyridine and terphthalic acid

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ABSTRACT

The resin, DAPT, was synthesized by condensing 2, 6-Diaminopyridine (0.1M) and terphthalic acid (0.1M) in presence of DCC (Dicyclohexylcarbodiimide). The tentative structure of resin was assigned by elemental analysis, ¹H NMR, ¹³C NMR, FT-IR and UV-VIS spectra. The molecular weight of resin was determined by non aqueous conductometric titration. The thermo kinetic parameters such as apparent entropy (ΔS), frequency factor (A), free energy change (ΔG) and orders of reaction were determined by Freeman Carroll (FC) and Sharp Wentworth (SW) methods. The order of degradation determined by FC method was confirmed by SW method.

Keywords: Polycondensation, Copolymer, Thermal properties, Resin, Thermokinetic parameters.

INTRODUCTION

Copolymers have a great potential and offer challenges for new technology and growth into the twenty-first century. Recently there has been growing interest in finding new applications for available polymers along with their derivatives [1-6]. Copolymers useful applications as adhesives and coating in electrical sensors, high temperature flame resistant, fibers, coating materials, semiconductors, catalysis, ion exchange resins, electrical insulation, heat and chemical resistivity and thermal stability [7-12]. Literature survey has been revealed that various workers have shown immense interest in improving thermal stability. 2, 6 Diaminopyridine was used in fluorometric studies of novel photoactive polyamide [13]. The derivatives of pyrene, other condensed aromatic hydrocarbons and some heteroaromatic hydrocarbons such as pyrazoline are more considerable in the preparation of photoluminescence polymers [14]. Many coworkers reported the use of 2, 6 diaminopyridine in synthesis macro cyclic ligand for chelation with metal ions such as Ni(II), Cu(II), Cr(III), La(III), Pb(II), Cd(II), Zn(II) which obviously open up fascinating area of research in coordination chemistry [15-16]. Various efforts were made by polymer chemist to improve the properties of resins by changing monomer composition in light of industrial applicability in spite of difficulties of low processability and thermal instability. Thermogravimetric study of polymer provides information about the degradation pattern during heating and thermal stability. Gurnule have reported thermodynamic parameters and order of thermal stabilities of copolymers by using TGA [17]. Some recent development have made in the field of thermally stable polymers that have grown very rapidly to increase the applicability at elevated temperatures. However the polymer chemists have to face the challenges due to thermal instability and low processability. In this connection many co-workers have made attempt to improve thermal stability by changing the composition of monomers [18]. Masram reported kinetic study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde [19].

The kinetics of degradation can generate parameters, which can be subsequently used to deduce the lifetime of polymers at different temperatures [20]. It is almost impossible to obtain the exact kinetic parameters for each reaction involved in the polymer decomposition and apparent kinetics parameters are often used to represent the behavior of polymer decomposition in general [21]. Actually these parameters rather represent the overall weight loss behavior during the thermal decomposition as a function of temperature. Hence in literature several methods have been reported for the determination of kinetic parameter from thermal analysis [22]. Many co-workers determined various kinetic parameters such as ΔS , A and ΔG by using Freeman Carroll and Sharp -Wentworth method [23-25]. The present paper deals with the structural analysis of newly synthesized copolymeric DAPT resin and its thermal study using following methods [26-27].

A) Freeman-Carroll Method: In this method activation energy and order of degradation is related with following expression,

$$\frac{\Delta \log(dw / dt)}{\Delta \log W_r} = \left[-\frac{Ea}{2.303 R} \right] \times \frac{\Delta(1/T)}{\Delta \log W_r} + n \dots (1)$$

Where

dw/dt = Rate of change of weight with time

W_r = Difference between weight loss at completion of reaction and at time t

Ea = Activation energy

n = Order of reaction

B) Sharp-Wentworth Method: Following expression has been used to evaluate the kinetic parameters.

$$\log \frac{(d\alpha / dt)}{(1 - \alpha)^n} = \log \frac{A}{\beta} - \frac{Ea}{2.303 RT} \dots (2)$$

Where

$d\alpha/dt$ = fraction of weight loss with time

n = Order of reaction

A = Frequency factor

β = Linear heating rate

α = Fraction of amount of reactant

MATERIALS AND METHODS

Materials

Chemicals were obtained from Merck, Qualigens and S.D. Fine in AR and chemically pure grade.

Synthesis of DAPT copolymer Resin

The DAPT copolymer was prepared by condensing 2, 2-diaminopyridine (0.1M) and terephthalic acid (0.1M) at 70°C in oil bath for 9.00 hours with intermittent shaking. The pale white colored product so obtained was repeatedly washed with hot water to remove unreacted materials. The copolymer was dried and powdered. The product was washed with 0.1N HCl to remove unreacted 2, 6-diaminopyridine followed by several washings with hot water. It was further purified by dissolving in 2% NaOH then filtered and reprecipitated by gradual drop wise addition of 1:1 HCl with constant and rapid stirring in order to avoid lump formation. The DAPT copolymer so obtained was washed several times with hot deionized water and dried in vacuum. The purified copolymer was finely ground to pass through 300 mesh size sieve and kept in a vacuum over silica gel. The yield of the copolymer was found to be about 74%. The reaction scheme for synthesis of DAPT is shown in figure 1.

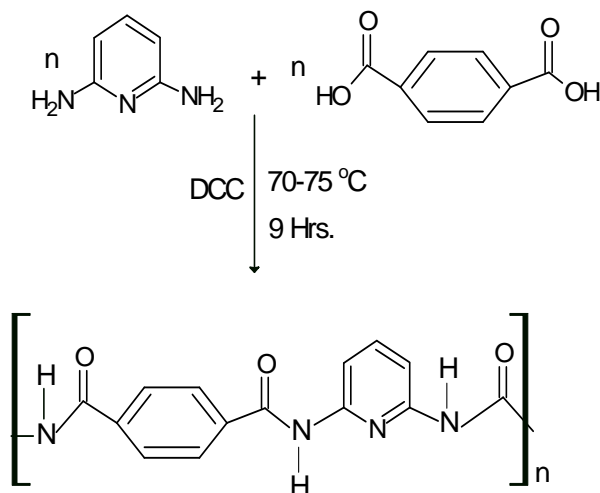


Figure 1. A reaction scheme –synthesis of DAPT

Table 1. Synthetic details of DAPT resin

parameters/conditions	Specifications
Copolymeric ligand	DAPT
2,6 Diaminopyridine	0.1M
Terphthalic acid	0.1M
Catalyst (DCC)	10 g.
React.Temp	70 °C
Time	9.0 hrs
Yield	74%

RESULTS AND DISCUSSION

Elemental Analysis and molecular weight of DAPT resin

The elemental analysis (C, H, and N) of copolymeric resin was carried out at Sophisticated Analytical Instrumental Facility (SAIF), Indian institute of Technology (IIT) Bombay. The average degree of polymerization of resin sample was determined by titrating 25ml of 0.1% solution of resin in DMF against 0.1M KOH solution in absolute alcohol, conductometrically [28]. The conductance was plotted against the milliequivalents KOH per 100gm. of resin. The inspection of plot revealed that there were many breaks in the plot. The DP was calculated by using following equation,

$$\overline{DP} = \frac{\text{Milliequivalent of base required for complete neutralisation}}{\text{Milliequivalent of base required for smallest interval}} \quad (3)$$

The molecular weight of repeating unit was determined from elemental analysis data as shown in following table 2. The molecular weight of resin was determined by using following relation,

$$M_n = DP \times \text{Molecular weight of the repeating unit} \quad \text{-----} \quad (4)$$

The repeating unit weight was obtained from elemental analysis.

The elemental analysis and molecular weight determination data of DAPT resin are given in following Table 2.

Table 2. Elemental Analysis and molecular weight determination of DAPT resin

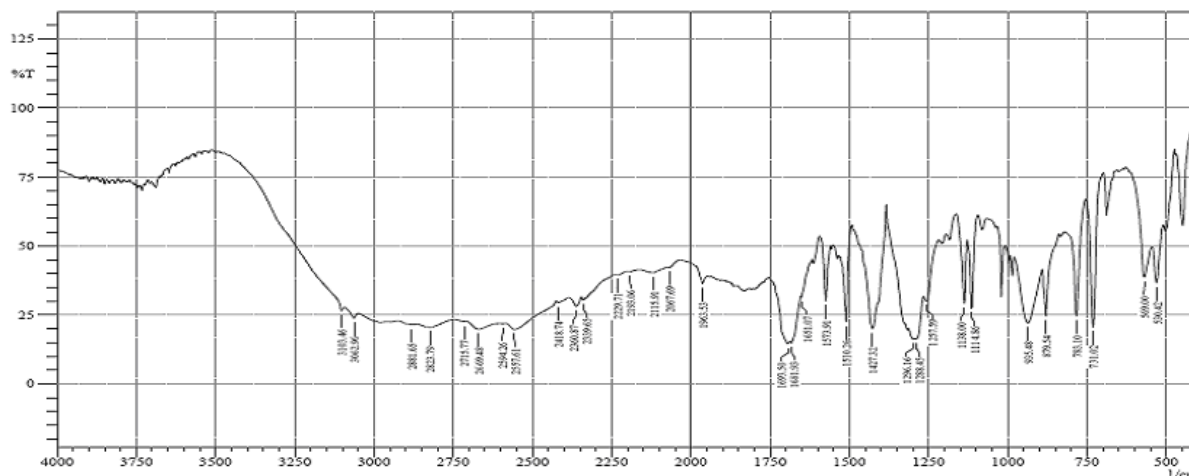
Resin	%C		%H		%N		DP	Molecular weight (M _n)	Mol. Formula of repeating unit	Molecular Weight of repeating unit
	Cal	Found	Cal	Found	Cal	Found				
DAPT	59.57	58.94	3.54	3.43	19.85	19.65	17	4794	C ₁₄ H ₁₀ N ₄ O ₃	282

Spectral analysis

FTIR spectra of synthesized copolymeric resins were recorded at Department of pharmacy; RTM Nagpur University, Nagpur Using FT-IR spectrophotometer Shimadzu, Model No-8101A. ¹H and ¹³C NMR spectrum of copolymeric resin using DMSO-d₆ solvent was scanned on BRUKER AC II 400 NMR spectrophotometer SAIF, Punjab University, Chandigarh. UV-VIS spectra of copolymer resin in DMSO solvent recorded by UV-VIS Double Beam Spectrophotometer Shimadzu, Model No-1701 fitted with automatic pen chart recorder at Department of Pharmacy, RTM Nagpur University, Nagpur.

FTIR spectrum data of DAPT resin

FT- IR spectra are shown in figure 2 and data are tabulated in table [29-30].

**Figure 2. FTIR spectrum of DAPT resin and peak assignments****Table 3. FTIR Spectrum data of DAPT resin**

Frequency in cm ⁻¹	Nature of fragment assigned	Frequency in cm ⁻¹	Nature of fragment assigned
3103	NH Str. in sec. amide	1510	Sec. amide (II) band
3062	CH Aromatic str.	1427	C=N Str. (pyridine ring)
2339,2360,2418	Overtone bands	1296,1288	C-N Str. in -CONH-
1691	C=O amide(I) band	1020,997	C-O deformation in -CONH-
1651	C=C (Pyridine ring Str.)	879	1,4 disubstituted aromatic ring
1573	N-H deformation	1114,1112, ,783,731	1,6 disubstituted pyridine ring

The absorption band at 3103 cm⁻¹ was assigned to N-H stretching in secondary amide. The broad band at 3062 cm⁻¹ was assigned to C-H aromatic stretching. The absorption at 1691 cm⁻¹ was assigned to >C=O amide (I) band. Further low value of this band was supported to formation of polyamide. The band at 1510 cm⁻¹ is due to the coupling of N-H bending and C-N stretching absorption (amide II band) indicates the presence of secondary amide group (amide linkages). The sharp band displayed at 1573 cm⁻¹ was assigned to N-H deformation. The band display at 1651 cm⁻¹ was assigned to C=C in pyridine ring. The absorption at 1427 cm⁻¹ was attributed to C=N stretching in Pyridine ring. The band display at 1296, 1288 cm⁻¹ was assigned to C-N stretching in secondary amide.

The peaks at 1020, 997 cm^{-1} are due to C-O deformation in -CONH-. The peaks at 879 cm^{-1} was assigned 1, 4 disubstituted aromatic rings. The peaks at 1114, 1112, 783, 731 cm^{-1} was assigned to 1, 6 disubstituted pyridine rings.

^1H NMR and ^{13}C NMR Spectrum of DAPT resin

The ^1H NMR and ^{13}C NMR spectrum is shown in figure 3 and figure 4 respectively.

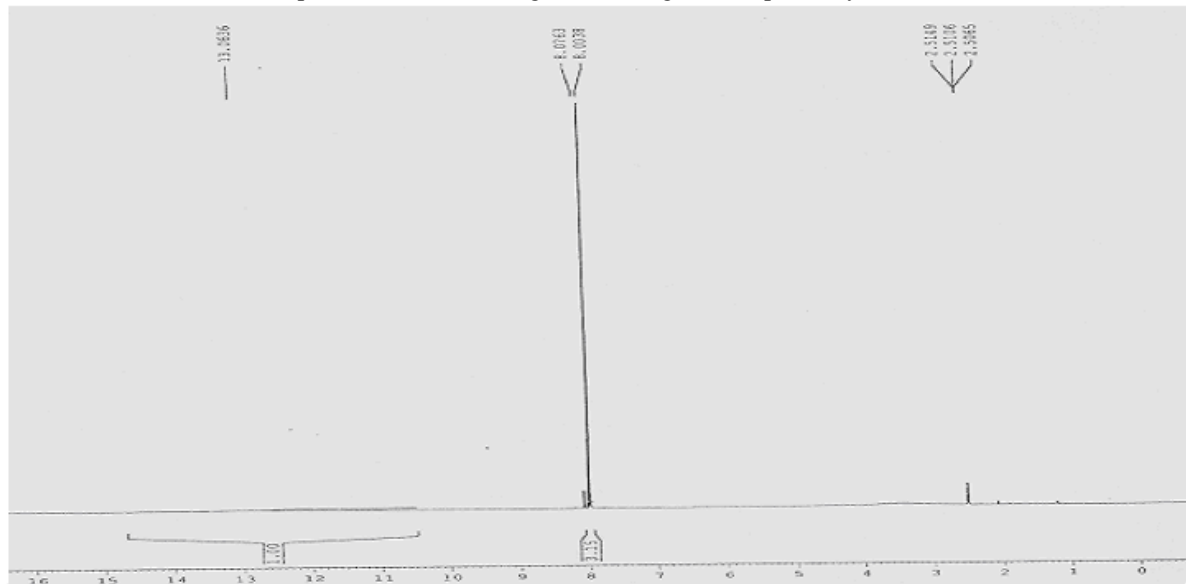


Figure 3. ^1H NMR spectrum of DAPT resin

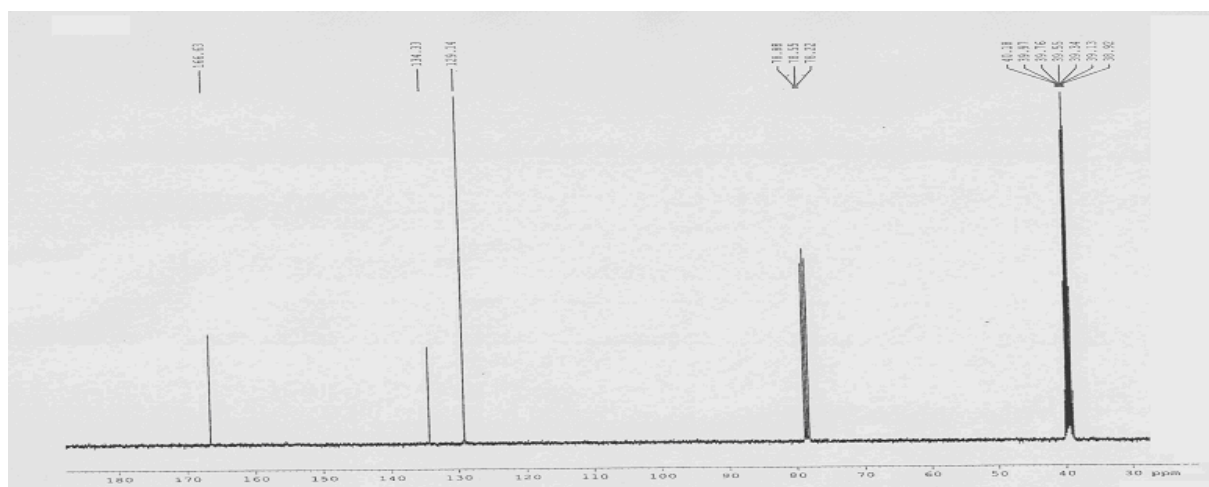
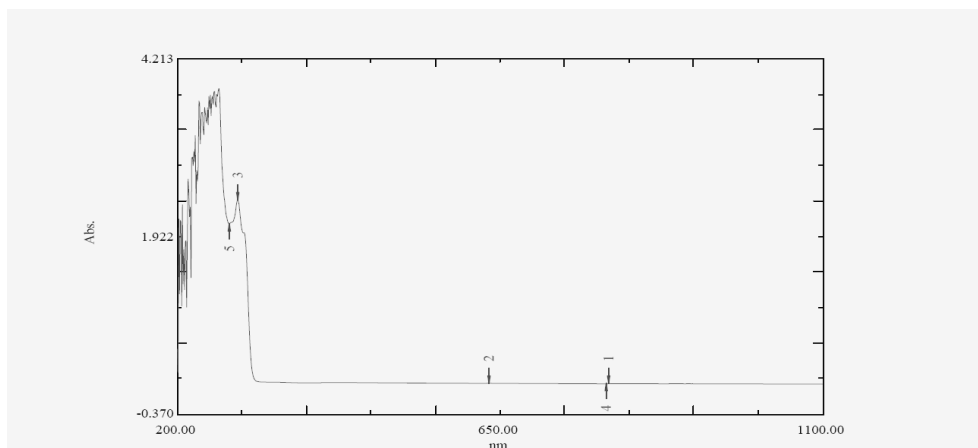


Figure 4. ^{13}C NMR spectrum of DAPT resin

In ^1H NMR spectrum of DAPT copolymer the signals at 8.0 δ ppm was attributed to N-H in amide linkages. The signal at 8.07 δ ppm was due to proton in pyridine ring. The signal at 2.50 δ ppm was due to DMSO solvent. In ^{13}C NMR spectrum of DAPT copolymer the signal at 129.14 δ ppm was assigned to carbon in terphthalic acid moiety. Signal at 134.33 δ ppm are due to carbon in pyridine ring. Signal at 166 δ ppm was attributed to $>\text{C}=\text{O}$ carbonyl carbon in amide linkages [31-32].

UV-VIS spectrum of DAPT resin

The UV-VIS spectrum is shown in following figure 5 Inspection of UV-VIS spectrum of DAPT resin reveals two types of transition $\pi-\pi^*$ and $n-\pi^*$ transition. The important UV-VIS absorptions are tabulated in table 4. [33].



5.

Figure 5. UV-VIS spectrum of DAPT resin

Table 4. UV-VIS data of DAPT resin

Resin	Transition	Wavelength (nm)	Group/ moiety assigned
DAPT	$\pi-\pi^*$	234	C=C Aromatic ring
		253	C=N Pyridine ring
		267	C=C Pyridine ring
	$n-\pi^*$	284	C=O amide group
		295	pyridine ring

Thermo gravimetric analysis of DAPT copolymeric resin

The thermo gram of DAPT copolymer resin as shown in figure 6 was recorded at Dept. of Material Science, VNIT Nagpur, using Perkin Elmer Diamond TGA/DTA analyzer in argon environment. The resin was allowed to heat up to 800°C at linear heating rate of 10°C min⁻¹. The initial weight loss up to 150°C was due to the loss of waters. The decomposition of resin starts from 513 to 613 K. The order of decomposition was found to be 0.46 orders by Freeman-Carroll method, which was further confirmed by Sharp- Wentworth method. The FC and SW method plots are shown in figure 7 and figure 8 respectively. The thermo kinetics parameters determined by these two methods are shown in table 5. [34-35].

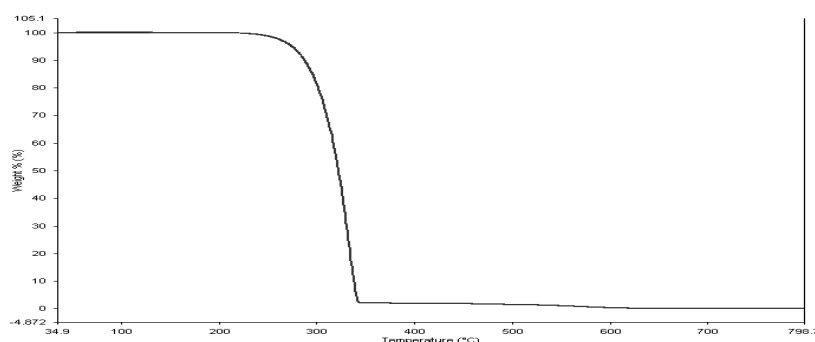


Figure 6. Thermogram of DAPT resin

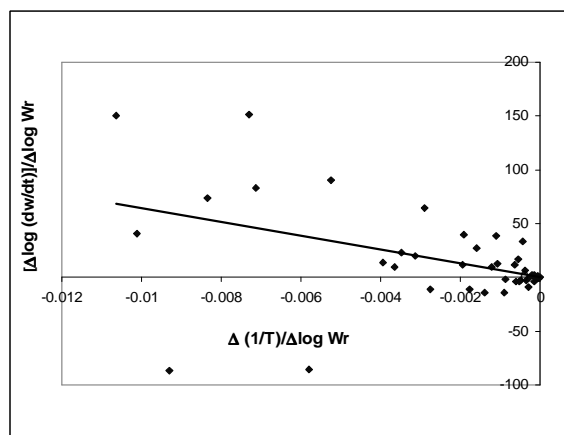


Figure 7. Freeman- Carroll plot of DAPT resin

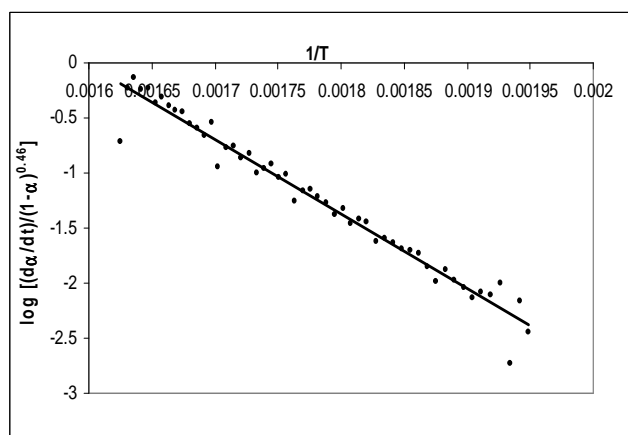


Figure 8. Sharp -Wentworth plot of DAPT resin

Table 5. Thermo kinetic parameters of DAPT resin

Resin	Parameters	Freeman-Carroll method	Sharp-Wentworth method
DAPT	Temperature range	513 - 617 K	513 - 617 K
	Activation energy, Ea (kJ)	135.54	128.96
	Frequency factor, A (min ⁻¹)	7.621 x 10 ¹¹	5.689 x 10 ¹¹
	Apparent entropy, ΔS (JK ⁻¹)	-53.38	-50.96
	Free energy, ΔG (kJ)	167.30	159.28
	Order of reaction, n	0.46	0.46

CONCLUSION

The elemental analysis and spectral studies such as UV-VIS, IR, ¹H NMR, ¹³C NMR data is in good agreement to the above assigned tentative structure of DAPT copolymer shown in figure 2. The activation energy obtained by FC method is slightly higher than that obtained by SW method. The values of frequency factor, apparent entropy and free energy are in good agreement. The order of degradation reaction is in a fraction (0.46) due to solid state degradation. The low value of activation energy and high value of frequency factor suggest that the resin is thermally unstable between above mentioned temperature range. Similarly low value of entropy change suggests well ordered structure of copolymer. The copolymer may be used macro cyclic ligand as well as chelating ion exchanger due to donor N atoms.

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