

## **Rapid High Temperature Amidation in Presence of Organic Phosphites**

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### SUMMARY.

When reacted for periods of the order of 5 to 10 minutes at temperatures approaching 300°C in the presence of certain organic phosphites, polymers containing available carboxy and aliphatic amine groups undergo amidation. Thus, when aliphatic polyamides having amine and carboxy end groups are reacted with themselves in this manner, large increases in their molecular weight rapidly take place. When carboxy-containing polymers are reacted with other, aliphatic amine-containing polymers, block or graft copolymers are obtained.

### INTRODUCTION.

The use of aryl phosphites together with organic bases such as pyridine or imidazole to prepare aliphatic or aromatic polyamides was reported (1-8). Such reactions are conducted at close to ambient temperatures for aliphatic polyamides and up to about 120°C for aromatic polyamides. The polymerizations are carried out in N-methylated amide solvents such as N,N-dimethylacetamide or N-methylpyrrolidone, in the presence of inorganic chlorides such as LiCl or CaCl<sub>2</sub>. These salts enhance the solubility of the polymeric product in the reaction mixture and, as a result, increase its molecular weight. In general, the molecular weight of the aromatic polyamides far exceeds the rather low molecular weight of aliphatic polyamides prepared in this fashion. The molecular weight of the aromatic polyamides is temperature dependent, peaking at a polymerization temperature of about 85°C (3) and is rapidly decreasing above 110°C.

Melt polymerizations of polyamides usually require inert gas sweep, while chain extension in the solid state is carried out at elevated temperatures, below the polyamide melting point, under high vacuum. It is claimed in the patent literature (9,10) that the addition of small amounts of certain organic phosphites increases somewhat the molecular weight of the polyamide products.

In this preliminary communication we wish to report a high temperature amidation of polymers containing carboxy and aliphatic amine end-groups, made possible by the presence of organic phosphites (11-14). The reaction is different from the above in that it is very rapid and may take place during the few minutes it takes to extrude molten polymers. The reaction proceeds very well with aliphatic amines and to

a much lesser extent with aromatic ones. It requires no vacuum or inert gas sweep, and uses neither organic base nor solvent. The reaction seems not to proceed below 200°C, to be rather sluggish at about 225°C and to gradually increase its rate to become rather rapid at the convenient melt processing temperature interval of about 265°C to 315°C.

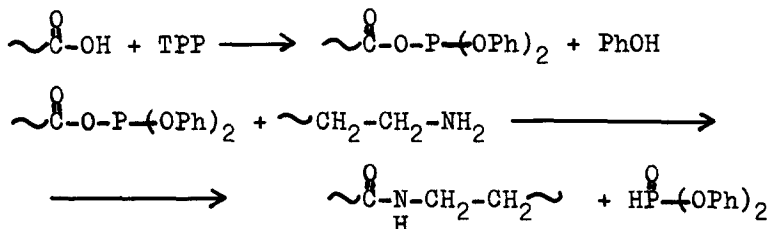
#### EXPERIMENTAL.

All reactions were conducted in a 1" Wayne extruder equipped with an L/d = 24 single stage screw. Polymers were pre-dried in vacuum ovens for at least 16 hrs at 100°C and above. After drying, organic phosphites in the range of 0.5% to 1% by weight were usually added to the minor polymeric component, the mixture tumble-mixed and immediately added to the major component and mixed again. When a polymer was reacted with itself, the phosphite was added to the pre-dried polymer and tumble-mixed only once. Care was taken to have all polymeric components in the same physical form: either both as pellets or both as coarse powder. The mixture was then fed through the extruder; the extrudate passed through a water trough to cool, then chopped in a pelletizer and dried in vacuum ovens at 110°C prior to further use. The residence time and nominal temperature in the extruder were predetermined by setting the screw rpm and the heaters in the four heating zones. For most analytical purposes the extrudate pellets were ground in a standard model No. 3 Wiley mill at Dry Ice or liquid nitrogen temperatures.

Relative and intrinsic viscosity measurements of the starting polymers and the extrudates (with or without phosphites) were found to be a rapid method to determine whether a reaction took place during extrusion. In the case of a single polymer reacting with itself, a substantial increase in the solution viscosity was sufficient to demonstrate that a chain extending reaction was achieved. When two polymers were expected to react, viscosity measurements were insufficient by themselves, and selective fractionations of the pulverized extrudates aided by centrifugation, were conducted. The collected fractions were then analyzed by elemental analysis, end-group titration and spectroscopic techniques such as IR, NMR and x-ray diffractometry, as is customary in the art. In all cases but one (polycapramide (nylon-6)/poly(hexamethylene adipamide)(nylon-66)), a fraction insoluble in solvents for both parent polymers could be collected. Furthermore, analysis of the polymers retrieved from the respective solutions indicated that in most instances minor amounts (on the order of 10%) of the insoluble polymers were carried into solution by the soluble polymers. Neither such behavior nor the appearance of an insoluble fraction were observed in polymeric mixtures extruded in the absence of phosphites. In the case of nylon-6/nylon-66, where the solubility characteristics of the polymers are identical, measurements of melting point changes by means of DSC and variations in crystal habits, detectable by x-ray analysis, were instructive.

RESULTS AND DISCUSSION.

Analysis by FTIR and phosphorus NMR of the polymeric reaction products and, especially, low molecular weight model compounds, revealed that the amidation reaction can be written as:



where TPP stands for triphenylphosphite, Ph stands for phenyl and typical reaction conditions are 5 minutes at 280-300°C. It should be noted that several additional phosphorus-containing by-products were detected in small quantities, most likely originating from oxidation and/or repeated participation in the above reaction. Under identical conditions attempts to amidate aromatic amines yielded only small amounts of amide linkages.

From the above one finds that when a single polymer having carboxy and aliphatic amine end-groups reacts with itself one obtains chain extension and increased molecular weight. When two polymers, respectively containing carboxy and aliphatic end-groups react with each other, a block or graft copolymer is obtained. Commercial polyamides, in general, contain both amine and carboxy end-groups. Therefore, when such a polyamide is reacted with another polymer, it may also react with itself in a competing reaction. Thus, an increase in the viscosity of the reaction product, as compared to a blank exposed to the same processing conditions, does not necessarily mean that block or graft copolymer was obtained, and fractionation followed by characterization of the fractions is necessary.

Under otherwise identical conditions, using the same mol-% phosphite and nylon-6 of  $M_n=19000$  with about equal number of amine and acid end-groups, it was found that the efficiency of the organic phosphites in increasing the molecular weight of aliphatic polyamides is: triphenyl phosphite > diphenyl phosphite > trisnonylphenyl phosphite  $\approx$  tributyl phosphite (TBP)  $\geq$  tris(di-t-butylphenyl)phosphite > trichloroethyl phosphite  $\geq$  triisodecyl phosphite  $\geq$  diphenylisodecyl phosphite > bis-2,4-di-t-butylphenyl pentaerythritol diphosphite > triethyl phosphite  $\gg$  distearyl pentaerythritol diphosphite. Inorganic phosphites such as calcium hypophosphite and phosphorous acid proved to be completely ineffective in promoting the amidation reaction under the conditions described above.

Typical single polymer reaction results are shown in Table 1. Block or graft copolymer formation was demonstrated for the systems in Table 2. For most systems more than one component ratio was tried. When phosphites were not used, only a very small amount of block formation between nylon-6

Table 1.  
Molecular Weight Enhancement of Single Polyamides.

Polymer	Phosphite Reaction		Relative viscosity	refs.	
	%	time			
Nylon-6	0	10	265	1.85	12
Nylon-6	0	5	300	1.84	12
Nylon-6	1% TPP	15	200	1.84	12
Nylon-6	1% TPP	10	245	2.00	12
Nylon-6	1% TPP	7.5	265	2.24	12
Nylon-6	1% TPP	3.75	285	2.57	12
Nylon-6	1% TPP	3.75	305	3.98	12
Nylon-66	0	7.5	300	1.66	12
Nylon-66	0.6%TBP	7.5	300	2.41	12
Polyundecanoamide <sup>b</sup>	0	5	300	1.38	13
Polyundecanoamide	1% TPP	5	300	2.17	13
Polylauro lactam <sup>c</sup>	0	5	300	1.36	13
Polylauro lactam	1% TPP	5	300	2.06	13

(a) Time in minutes, temperature in °C, relative viscosity at 0.5% concentration in m-cresol.

(b) Nylon-11. Amidation occurs only above 285°C.

(c) Nylon-12. Amidation occurs only above 285°C.

Table 2.  
Block or Graft Copolymers Formed Within 5 min at 300°C  
in Presence of 1% TPP.

Polymer pair	Ratios employed	refs.
Nylon-6/Nylon-66	1:1,85:15	12
Nylon-6/Nylon-12	85:15,95:5	13
Nylon-6/Nylon-11	85:15,95:5	13
Nylon-6/Poly(hexamethylene -terephthalamide) <sup>a</sup>	85:15,95:5	11
Nylon-6/Poly(trimethyl -hexamethylene tere- -phthalamide) <sup>b</sup>	85:15,90:10,95:5	13
Nylon-6/Poly(ethylene -terephthalate)	1:1,80:20,85:15,95:5	11,14
Nylon-6/Poly(butylene -terephthalate)	1:1,85:15,90:10,95:5	11,14
Nylon-6/Poly(cyclohexyl -dimethylene tere/iso -phthalate) <sup>c</sup>	85:15,90:10,95:5	11,14
Nylon-6/Poly(ethylene-co- -acrylic acid)	80:20,85:15,90:10	11
Nylon-6/ionomers <sup>d</sup>	80:20,90:10	11

(a) Nylon-6T. (b) Trogamid T of Dynamit Nobel A.G.

(c) Kodar A150 of Eastman Chemical Products Inc.

(d) Surlyn 1855 and Surlyn 1856 ionomers of E.I. duPont de Nemours, Inc.

and nylon-11 was evidenced among all difunctional polymers, and some grafting took place between nylon-6 and the polyfunctional ionomers and poly(ethylene-co-acrylic acid). The levels of grafting were far smaller than in the presence of organic phosphites. As indicated above, proof of the block

or graft formation was obtained by the combined use of fractionation and analytical techniques. Detailed analysis and discussion of the results are soon to appear.

#### CONCLUSIONS.

The results indicate that the amidation reaction in the presence of organic phosphites is expected to proceed under the conditions described above, provided that (a) the participating polymers, polyamides or others, contain available aliphatic amine and carboxy groups, (b) they are stable under said conditions, and (c) they are molten under these conditions and their melt viscosities are sufficiently close for thorough mixing in the molten state.

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