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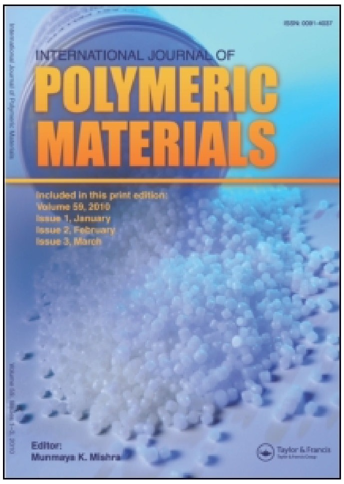

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Polycondensations in the Presence of Aromatic Phosphites: Conditions and Reaction Products

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Polycondensations in the Presence of Aromatic Phosphites: Conditions and Reaction Products

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Aromatic phosphites drive two kinds of condensation reactions: amidation and esterification. The amide-forming reactions are far more efficient, lending themselves to polymerization as well as chain extension. The ester-forming reactions are significantly more sluggish, limiting their usefulness to the extension, grafting, or block copolymerization of appropriately terminated pre-existing polymer chains. Polyamidations under Yamazaki conditions are most effective over the range of $85 < T < 115°C$. Here, in certain aprotic amide solvents such as *N,N*-dimethylacetamide (DMAc), aromatic amines rapidly, and certain aliphatic amines slowly, condense with carboxylic acids in the presence of aryl phosphites and organic bases to form amide groups. Typical of these phosphites is triphenylphosphite (TPP) and typical of the bases is pyridine. Under these conditions ester formation or breakup do not take place. Examples of the versatility of this procedure are given. Monomers reactive under Yamazaki conditions, and those that fail to react, are listed and discussed. At the temperature interval of $120 < T < 155°C$, the efficiency of amidation of aliphatic amines approaches that of aromatic amines. In this case the solvent is DMAc or DMAc/LiCl or *N*-methyl-2-pyrrolidinone (NMP). TPP and pyridine are present, the latter under reflux. Under these conditions, grafts of high molecular weight aliphatic polyamides were created, reacting aliphatic carboxylic acids with aromatic amines and, conversely, aromatic acids with aliphatic amines. The graft efficiency is rather high. Above the boiling point of the aprotic amide solvents, no solvent or organic base are used. Here, aryl phosphite alone is employed to create aromatic amines, aliphatic amides, polyamide chain extension during extrusion, and block and graft copolymers containing aliphatic amide linkages. Esterification reactions occur at even higher temperatures. Chain extension of poly(ethylene terephthalate) (PET) was achieved in both extruder and melt-processor at temperatures of 265°C and higher, but at rates far slower than for polyamides.

KEY WORDS Polymerizations, polycondensations, phosphite, polyamides, polyesters

INTRODUCTION

A first indication of the potential of triarylphosphites as condensing agents was given a generation ago by Mitin and Glinskaya.[1] Aliphatic amino acids were dimerized to form peptides by dissolving them in suitable solvents, preferably *N,N*-dimethylformamide (DMF) or dioxane, and conducting the condensation reaction in the presence of triphenylphosphite (TPP) and imidazole for 18 hrs at 40°C. In addition to the peptide, the by-products diphenylphosphite (DPP) and phenol were found in the reaction mixture.

This reaction was extended by Ogata and Tanaka[2] to room temperature polycondensation reaction of ω-amino acids and equimolar salts of diamines and dicarboxy acids to obtain low molecular weight polyamides. In this case, it was found that the solvents giving the highest polyamide yield were DMF and *N,N*-dimethylacetamide (DMAc) and that in the case of aromatic monomers, the addition of some anhydrous LiCl increased the solubility of the polymeric products and contributed to the enhancement of the molecular weight. Despite the fact that reaction times exceeded 40 hrs, the reduced viscosity surpassed 0.2 dL/g only once.

Yamazaki and associates refined the polycondensation by first realizing that pyridine is a far better co-reagent than imidazole[3,4] and then determining that about 4 wt/vol percent LiCl (or 8 wt/vol % $CaCl_2$) in NMP was the best solvent mixture for polycondensation of aromatic monomers in the presence of TPP or DPP to give high molecular weight (high-M) aromatic polyamides.[5] In this work,[5] it was found that conducting the polycondensation for about 5–6 hrs at 80°C gave best results. Conducting the polymerization at 60°C gave only oligomers, while the polycondensations executed at 100°C or 120°C gave high-*M* polyamides whose molecular weight decreased with increasing temperature. Even at 80°C, 3 hrs and 10 hrs reaction times gave polymers with molecular weights lower than those obtained from 6 hrs reaction time.[5]

Over the past 15 years, I have conducted condensations in the presence of phosphites over a broad range of conditions. The reactions involved (a) the preparation of model compounds mostly for the purpose of elucidating the reaction mechanism, intermediates and by-products, (b) the preparation of linear, branched, star, and networks, of high-*M* polyamides, copolyamides and poly(ester amides), and (c) under rather restricted conditions, the preparation of polyesters. My observations will be reported below. They are divided into three broad categories according to the reaction temperature range and the medium in which each reaction is conducted. The specific details for each may be found in the cited references.

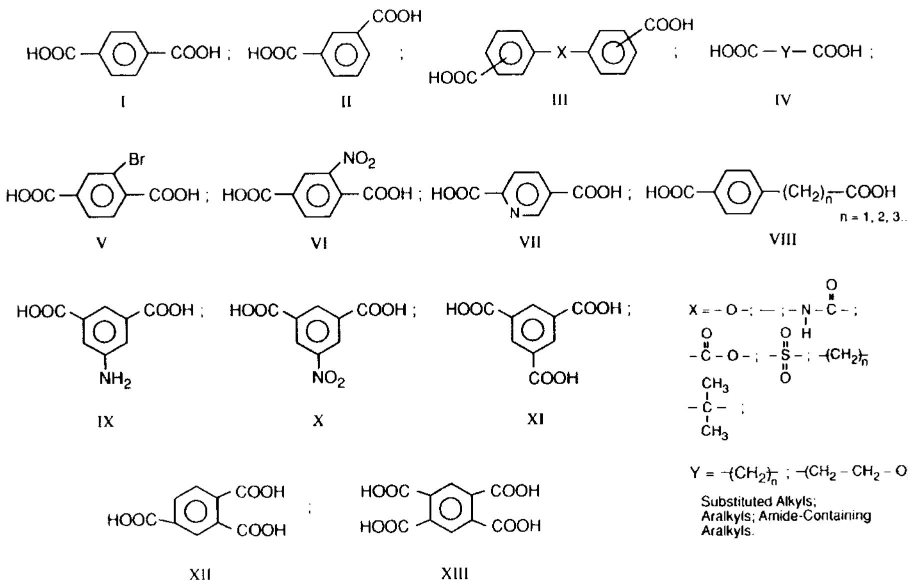
RESULTS AND DISCUSSION

Amide Formation Under Yamazaki Conditions[6–18]

By this, I mean condensation in solution and in the presence of TPP and pyridine. From all solvents tried, I found the aprotic amides to be most suitable for the reaction and from these, the best were MMP > DMAc > tetramethylurea > DMF. Except for this and one earlier study,[10] the reaction solvent for all polymerizations described herein was DMAc containing 5 wt/vol percent dry LiCl, or DMAc alone when the polymeric product was nicely soluble in it. Unlike Yamazaki *et al.*,[5] I have found that in DMAc/5% LiCl the best reaction temperature spans the interval $85 < T < 120$°C and, preferably, $90 < T < 115$°C. Within this range, the rate of polymerization greatly increased with temperature,[15] while the molecular weight of the polymeric products remained essentially unchanged. In stoichiometrical soluble systems, reaction time of about 60 to 90 minutes is sufficient to effect full monomer conversion. It is interesting to note that during efficient polycondensation at constant temperature, both monomer conversion and product molecular weight appear to be directly dependent on concentration.[10] At rather low concentration, the dilution appears to retard the reaction. At very high concentrations, polymer precipitation or solution microsyneresis greatly slow down the reaction. When the reaction was allowed a long time at temperature, the monomers finally were all consumed even though the molecular weight of polymers prepared at intermediate concentrations, ca. 10%, remains the highest.

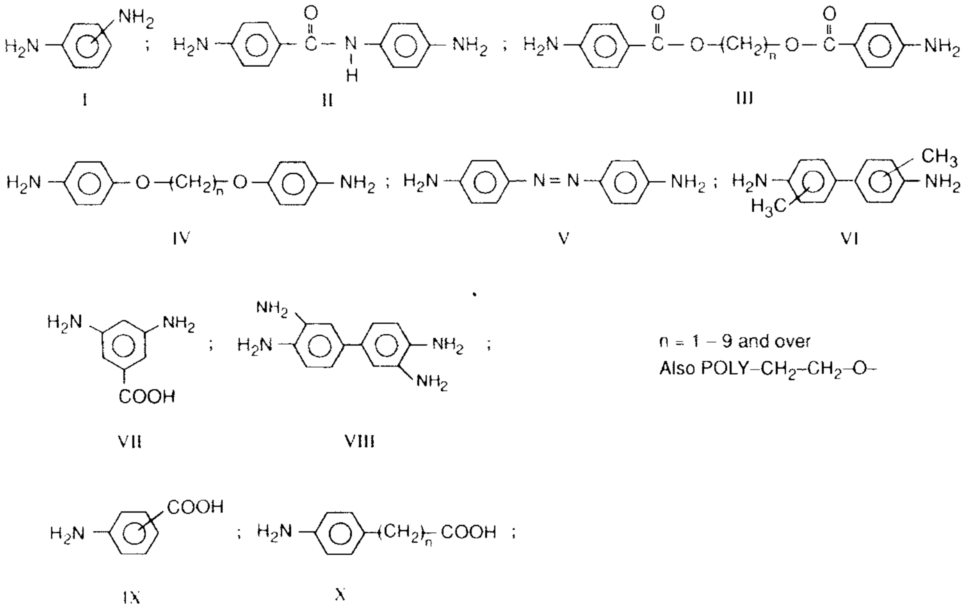
Ester groups remain unaffected under Yamazaki conditions. This allowed me over the years to create zigzag stiff aromatic poly(ester amides) in which all stiff segments are of identical composition and length,[11] flexible and semi-flexible gelled one-step networks,[8,9,15,16] gels of semi-flexible two-step networks,[18] and a large family of hydrogen-bonded strictly alternating thermotropic liquid crystal poly(ester amides).[14] These were made from monomers containing pre-formed ester groups. The liquid crystallinity of the strictly alternating poly(ester amides)[14] is unlike random or semi-random analogues[19] where no mesomorphicity exists. DSC, x-ray and NMR studies indicated the poly(ester amides) to be highly regular[20–23] and that no transesterification or transamidation occurred under Yamazaki conditions. Therefore, amide groups can be created from free carboxylic acids and aromatic amines under Yamazaki conditions in the presence of ester groups without the latter being affected. If, however, the reaction temperature is increased to, say, over 150°C, then the LiCl in the DMAc or NMP attacks the ester groups forming lithium carboxylate salts and chloroalkyl residues. In NMP/5% LiCl at 185°C, for instance, the reaction is highly efficient, reducing high-*M* poly(ethylene tere-

Easily Polymerizable Monomers Under Yamazaki Conditions: Carboxylic Acids



SCHEME I

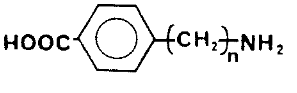
Easily Polymerizable Monomers Under Yamazaki Conditions: Aromatic Amines



SCHEME II

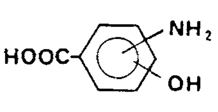
phthalate) (PET) to oligomers in a matter of minutes. In the absence of LiCl, this destruction does not occur. The selective attack of LiCl on esters at high temperature is similar to the selective cleavage of methyl esters by LiI reported in the literature.[24]

Monomer polymerizability is affected by their structure. Experimental results from my laboratory are shown in the following schemes. In Scheme I are shown aromatic and aliphatic diacids and aromatic polyacids easily polymerizable under Yamazaki conditions. In Scheme II are shown easily polymerizable aromatic amines and aromatic amino acids. The yields and molecular weights of polyamides prepared



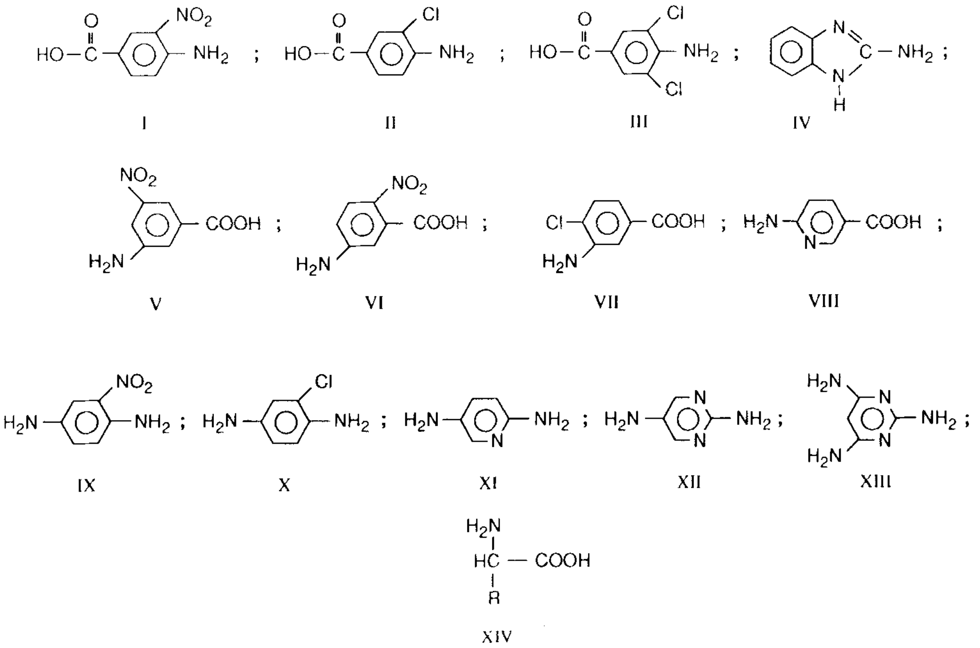
$n = 1,2,3$

greatly decrease with increasing *n*. Substituted aminophenols also show poor results:



Monomers that do not polymerize under Yamazaki conditions are shown in Scheme III. Comparison with Schemes I and II clearly shows that aromatic amines are much more prone to deactivation than aromatic carboxy acids. The presence

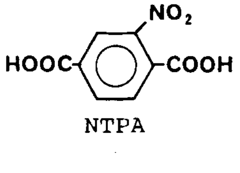
Monomers That Do Not Polymerize Under Yamazaki Conditions



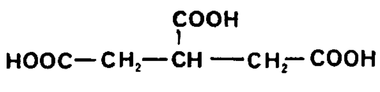
SCHEME III

of nitro group anywhere on the ring deactivates the aromatic amine but does not deactivate aromatic acids such as nitroterephthalic acid (NTPA). The presence of chlorine deactivates amine groups on the same ring, while the presence of bromine does not deactivate bromoterephthalic acid. The presence of nitrogen atom in an aromatic ring, such as in pyridine, pyrimidine or benzimidazole, deactivates amine groups attached to the ring but not carboxyl groups. Reactions of aliphatic diamines or α-amino acids were most often hindered by the formation of insoluble salts when the monomers were mixed in DMAc/5% LiCl[10] or by the rapid precipitation of low-*M* products once the reaction started.[4,10]

A very interesting situation involves the combination of the monomers NTPA and tricarballylic acid (TCA):



NTPA



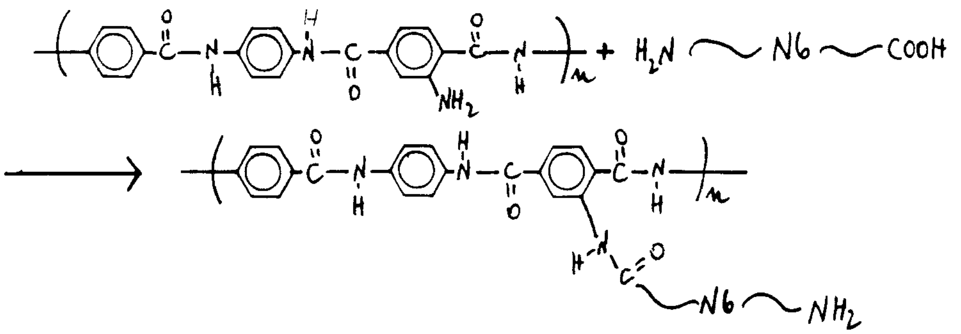
$$\mathrm{HOOC{-}CH_2{-}\overset{\displaystyle COOH}{\overset{|}{C}H}{-}CH_2{-}COOH}$$

TCA

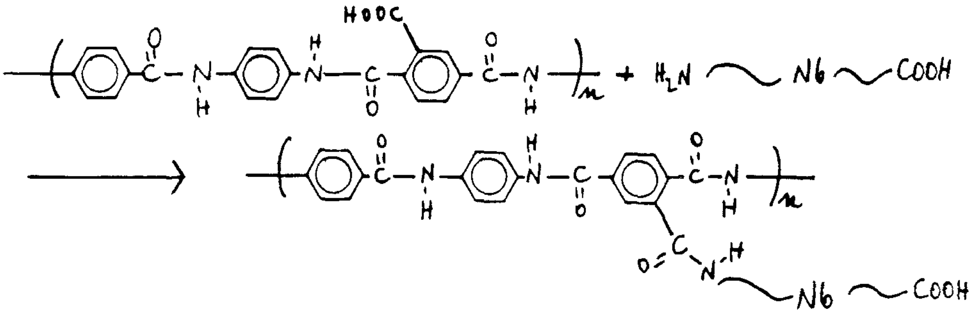
The two monomers, especially NTPA, polymerize very nicely with aromatic diamines to form high-*M* linear polyamides or well-formed low-defect networks when present in the reaction mixture in the absence of one another. The presence of other carboxy acids, such as terephthalic acid (TPA), 1,3,5-benzenetricarboxylic acid (BTCA) or sebacic acid, does not affect the reactivity of either NTPA or TCA.[9,15–17] However, when NTPA and TCA are present together, with stoichiometric amounts of aromatic diamines in the reaction mixture, no network is formed. Depending on the concentration, varying amounts of microgels appear in solution, but no "infinite," well-formed networks. The reasons for the unexpected behavior of NTPA and TCA in the presence of each other are not understood by me at present.

High Temperature Amide Creation in Solution[25]

I have found that in solution at the temperature interval of $120 < T < 155$°C, both aromatic and aliphatic amines participate in amide formation. Depending on the reactants and reaction products' solubility, the reaction solvent may be pure DMAc, DMAc/LiCl or NMP with or without LiCl. Pyridine is present in the reaction mixture, usually under reflux. The solutions of the reactants are prepared separately and TPP is carefully added to one and fully mixed in it before both solutions are mixed together. Depending on the concentration of reactive species, the reaction is allowed to proceed for 6 to 8 hrs, most commonly at about 130–135°C. Under these conditions grafts of high-M aliphatic polyamides and aromatic polyamides were created, reacting aliphatic carboxylic acid with aromatic amines and, conversely, aromatic acids with aliphatic amines.[25] The graft efficiency is rather high. Thus, for example, the carboxyl ends of high-M nylon-6 were grafted onto a stiff polyamide with aromatic amine groups at about 85% efficiency:



The grafting efficiency of aliphatic amines on aromatic carboxylic acids is not as high and reaches levels of only about 50% grafts:



It is worthwhile to mention here that the grafting of aliphatic carboxyl chain-ends onto the amine groups of stiff aromatic chains proceeds very well in the lower range of the reaction temperature interval, while the reaction of aliphatic amines with aromatic carboxy acids requires higher temperature. The bottom end of the temperature interval is dictated to a large extent by the solubility characteristics of the reactants. To prevent crosslinking, each flexible polymer chain to be grafted on the stiff ones must have only one chain-end capable of reacting with the stiff chains under the reaction conditions.

Amide and Ester Formation at Very High Temperatures in the Absence of Solvent and Pyridine

These reactions proceed very sluggishly at above 200°C but their rate greatly accelerates as we progress from ca. 250°C to 300°C and over. At any given temperature within this range, the formation of amide groups is much faster than the creation of esters. In fact, with increasing temperature care must be taken to prevent chain extension by esterification from being overtaken by polymer degradation.

The following types of condensation reactions were found to proceed in the presence of TPP or similar phosphites but in the absence of solvent, LiCl and pyridine:

(a) Block and graft copolymerizations of aliphatic polyamides with aliphatic and aromatic polyamides, or with polyesters, or copolymers of ethylene and acrylic acid; all obtained by mixing and reacting the starting polymers in the presence of phosphite in the molten state in an extruder or other melt-blending machines. Depending on the equipment used, the residence time is of the order of 2 to 10 minutes.[25,26,31–33]

(b) Chain extension of homopolymers, either polyamides or polyesters.[28,31–34]

(c) Quasi-random copolyamides from high molecular weight compatible homopolymers such as nylon-6 and nylon-66.[27]

(d) Preparation of low-*M* polyamide oligomers from their AB-type monomers, such as 4-aminobenzoic acid, 6-aminocaproic acid and 11-aminoundecanoic acid. At 280°C, the monomers are totally consumed in a matter of minutes.[32]

(e) Polyamide-polyester graft copolymer fibers.[30] The unique features of this process are: (i) The aromatic phosphite is compounded into the slower reacting polyester component in a separate preparatory step. (ii) The pellets of both components are thoroughly mixed and kept uniformly mixed throughout. (iii) The polymers are thoroughly mixed during the melt extrusion/spinning operation, preferably by the insertion of intensive static mixers into the melt stream. (iv) The spinning/reaction is conducted at around 285°C. (v) The phosphite is contained in the pellets of the slower reacting polymer in order to maximize the reaction between it and the rapidly reacting polyamide and, at the same time, minimize the self-reaction of the polyamide such that its melt viscosity not increase to force changes in processing conditions. (vi) The process lends itself to create grafted fibers of a range of polyamides and polyesters. (vii) Triphenylphosphite was found to be the most efficient, but other aryl phosphites such as diphenylphosphite, tris(nonylphenyl)phosphite, tri(2,4-di-*t*-butylphenyl)phosphite and many others were found to be highly effective.[28,30,31,33]

We believe the reactivity of aryl phosphites is caused by the aryloxy moiety being a good leaving group. This, in turn, is due to its ability to delocalize negative charges from the oxygen atom to the aromatic ring. Other good leaving groups with resonance capability include phosphines in which the trivalent phosphorus atom is connected by a single bond to a nitrogen atom in a five-membered heteroaromatic ring such as imidazole, pyrrole, pyrazole, indole, and carbazole. The leaving abilities of these groups are such that several of them serve as leaving groups in highly active phosphines for ambient temperature syntheses of peptides,[35] nucleotides, and their oligomers.[36,37] Additional groups capable, to some extent, of negative charge delocalization are aliphatic cyclic species containing one or two carbonyl groups adjacent to a nitrogen bonded to trivalent phosphorus atom. Here, the negative charge may resonate between the nitrogen atom and the carbonyl oxygen(s). Such potentially good leaving groups belong to the families of cyclic lactams and imides. A recent patent[38] describing the efficiency of tri(caprolactamyl)phosphine as polyamide chain-extending agent tends to support the above assertion.

It is interesting to note here that certain aromatic phosphates are also useful in increasing the molecular weight of aliphatic polyamides by coextrusion at temperatures of 260°C and higher, with residence of several minutes at temperature. From among the aromatic phosphates, tri(*p*-chlorophenyl)phosphate was found to be the most effective.[39]

CONCLUSIONS

Triarylphosphites are powerful reagents in condensing amines and carboxylic acids to form amide groups. The reactions in aprotic polar solvents proceeds rapidly in the presence of pyridine (under reflux when the reaction is carried at temperatures of 120°C and over) and their highest temperatures are limited by the boiling temperature of the solvents such as NMP and DMAc. While reactions with aromatic amines proceed very well in the range of $85 < T < 115$°C, reactions with aliphatic amines proceed at higher temperatures, about $120 < T < 155$°C. Some condensation reactions were successfully conducted in NMP at ca. 185°C. A broad array is presented of monomers reactive or inactive in solution polycondensations.

In the absence of solvent and pyridine, condensation and polycondensation reactions of monomers and polymers were found to increase in efficiency from about 250 to over 300°C. This allowed the creation in the extruder of polyamides and polyesters of molecular weights substantially higher than the starting materials, and a wide variety of block and graft copolymers.

Polycondensations in the presence of phosphites utilizes free carboxylic acids. In addition to the use of diacids and diamines, this allows the direct use in polycondensations of AB-type monomers without the need to convert them to the acid-chloride derivatives.

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