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Synthesis and Polymerization of N-Arylitaconimides: Free Radically and Anionically

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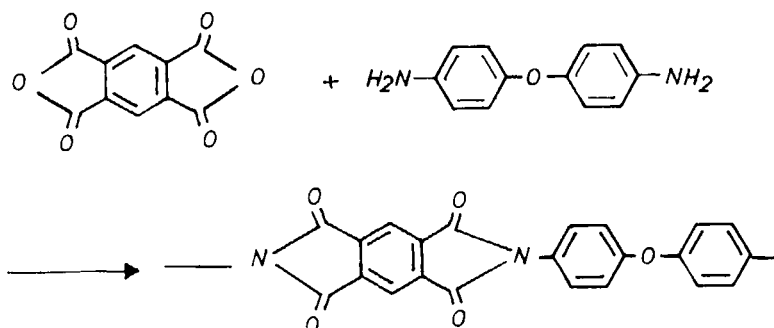
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ABSTRACT

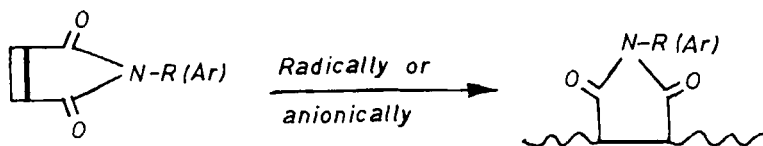
N-Phenyl-, N-p-tolyl-, N-p-methoxyphenyl, N-o-ethylphenyl-, and N-p-chlorophenylitaconimides were prepared from the corresponding itaconamic acids. These monomers were polymerized free radically to yield low molecular weight polymers. With the exception of N-p-chlorophenylitaconimide, all the above monomers polymerized anionically using n-butyllithium as initiator. N-o-Ethylphenylitaconimide formed a cross-linked polymer when polymerized anionically. The inability of N-arylitaconimides to produce high molecular weight polymers was attributed to the allylic hydrogens of the monomers.

INTRODUCTION

Cyclic imides and their N-substituted derivatives have been known as polymerizable compounds for some time. Polyimides prepared from several N-substituted imides proved to have high thermal stability [1] and high resistance to many chemical solvents [2, 3]. It is interesting to distinguish between two types of polyimides. One results from the condensation polymerization of monomers such as pyromalletic anhydride with a di-primary amine:



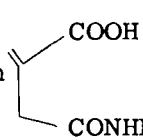
This type of polyimide is the sort of substance frequently referred to in the literature, and to which most of the good properties are attributed. The other type of polyimide, which is listed under the same entry in the literature, is produced by the addition polymerization of the vinyl group of an unsaturated imide such as maleimide or *N*-substituted maleimides:



Polymerization of *N*-substituted unsaturated cyclic imides through the vinyl group have been limited to several monomers [2-4]. This may be due to the difficulty of synthesizing new monomers in high yields and to the fact that the polyimides prepared so far have been of low molecular weight. Cubbon [5] prepared several polyimides using anionic and free radical polymerization of some *N*-substituted maleimides and reported their tacticity. *N*-Allylmaleimide [6] and *N*-allylcitraconimides [7] were cyclopolymerized to obtain polymers containing 70 and 85% cyclic repeating units, respectively. Marvel and Shepherd [8] reported the polymerization of itaconic acid and its esters. Nagai et al. [9] polymerized itaconic anhydride, while Akashi [10] copolymerized a few *N*-substituted itaconimides with vinyl acetate, methyl acrylate, and styrene. Recently Hartford and co-workers [11] prepared and polymerized two bis-itaconimides to obtain cross-linked polymers.

The conclusions drawn by some of the above investigators [8, 9] and by others [12, 13] clearly indicate the superiority of itaconic acid derivatives over maleic acid derivatives in homopolymerization reactions. However, little attention has been given to the homopolymerization of *N*-substituted itaconimides. This may be

TABLE 1. Melting Points, Percent Yields, and Elemental Analysis of Some N-Substituted Itaconamic Acids

R- in 	mp (°C)	% Yield	Elemental analysis					
			Calculated			Found		
			C	H	N	C	H	N
Phenyl	160-161	93	64.38	5.40	6.82	64.25	5.41	6.72
p-Methoxyphenyl	172-173	95	61.27	5.56	5.95	61.11	5.54	5.89
p-Tolyl	174-175	93	65.74	5.97	6.38	65.61	5.98	6.24
o-Ethylphenyl	142-143	87	66.93	6.40	6.00	66.87	6.44	5.91
p-Chlorophenyl	170-171	85	-	-	-	-	-	-
Allyl	104-105	85	56.70	6.50	8.20	56.67	6.53	8.14
Benzyl	146-147	90	65.70	5.90	6.38	65.68	4.96	6.18

partly attributed to the difficulty in their synthesis. N-Substituted itaconimides are known to isomerize readily to the corresponding N-substituted citraconimides at elevated temperatures [14]. In the present paper we report the synthesis and polymerization of several N-arylitaconimides free radically and anionically at different conditions.

EXPERIMENTAL

Preparation of N-Substituted Itaconamic Acids

N-Substituted itaconamic acids were prepared according to the procedure of Liwischitz et al. [15]. Tetrahydrofuran instead of ether was used to dissolve itaconic anhydride. Most of the amic acids produced were precipitated spontaneously after addition of the primary amine. However, some additional amic acid was left in the solvent, and it was obtained by the addition of some cyclohexane. The crude amic acids were purified either by recrystallization from cyclohexane or by dissolving them in dilute sodium bicarbonate solution followed by reprecipitation of the amic acids with dilute hydrochloric acid. Yields, melting points, and elemental analysis of the amic acids prepared are listed in Table 1.

TABLE 2. Melting Points, Percent Yields, and Elemental Analysis of Some N-Substituted Itaconimides

N-substituent	mp (°C)	% Yield	Elemental analysis					
			Calculated			Found		
			C	H	N	C	H	N
Phenyl	112-113	58	70.57	4.84	7.47	70.40	4.83	7.38
p-Methoxyphenyl	113	65	66.35	5.10	6.44	66.18	5.09	6.43
p-Tolyl	126	77	71.62	5.51	6.45	71.44	5.54	6.86
o-Ethylphenyl	78	47	72.57	6.08	6.50	72.55	6.09	6.40
p-Chlorophenyl	119	45	59.60	3.63	6.31	59.71	3.59	6.26
			Cl = 15.99			Cl = 15.95		

Preparation of N-Substituted Itaconimides

In a 250-mL round-bottom flask provided with a magnetic bar were placed 0.52 mol of N-arylitaconamic acid, 75 mL of dry acetone, 40 mL of acetic anhydride, and about 4 g of anhydrous sodium acetate. The mixture was refluxed for 2-3 h until a clear solution was obtained, according to the literature [11]. However, in some cases, e.g., the preparation of N-phenylitaconimide, a little precipitate remained after 3 h of refluxing. The solution was cooled to room temperature before pouring it into a beaker containing ice and water with vigorous stirring. A white precipitate of N-substituted itaconimide settled. The precipitate was filtered, then washed with cold distilled water several times before drying. The products were recrystallized from cyclohexane until a constant melting point was obtained. Following the above procedure, N-phenyl-, N-p-methoxyphenyl-, N-p-tolyl-, N-o-ethylphenyl-, and N-p-chlorophenylitaconimides were prepared. When acetic anhydride was added to an acetone solution of the amic acid, a turbid yellow solution formed in each preparation except in the case of N-p-tolylitaconimide where a purple solution was formed. The purple color gradually changed to pale green as refluxing continued. Yields, melting points, and elemental analysis of the imides prepared are listed in Table 2. Their NMR and major infrared absorptions are listed in Table 3.

Free Radical Polymerization of N-arylitaconimides

Ten grams of the pure monomer was dissolved in 60 mL of freshly distilled dry THF in a screw-capped polymerization bottle. An amount

TABLE 3. Nuclear Magnetic Resonance and Infrared Major Absorptions of Some N-Arylitaconimides

Compound	IR (cm ⁻¹)		NMR
	C=O	CH ₂ =C<	
N-Phenylitaconimide	1700	1660	(CDCl ₃) 7.44 (m, 5H, aromatic); 6.08 (d, J = 5 cps, 2H, CH ₂ =C); 3.53 (s, 2H, CH ₂)
N-p-Tolylitaconimide	1715	1665	(CH ₃ COCD ₃) 7.24 (m, 4H, aromatic); 6.10 (d, 2H, J = 6 cps, C = CH ₂); 3.55 (s, 2H, CH ₂); 2.45 (s, 3H, -CH ₃)
N-o-Ethylphenylitaconimide	1720	1665	(CDCl ₃) 7.40 (m, 4H, aromatic); 6.16 (d, J = 7 cps, 2H, CH ₂ =C); 3.55 (s, 2H, CH ₂)
N-p-Methoxyphenylitaconimide	1715	1665	-
N-p-Chlorophenylitaconimide	1715	1665	-

equal to 0.02% of the monomer's weight of azobisisobutyronitrile was added. The bottle was flushed with argon for few minutes inside a glove bag, and firmly stoppered. The clear solution was maintained at 55°C in a constant temperature oil bath for 4 h. The solution was then poured into about 150 mL of methanol to obtain a milky precipitate. The suspension was warmed to coagulate the colloidal product before filtration. The white precipitate was washed with methanol several times, dried in a vacuum oven overnight, and characterized. N-phenyl-, N-p-tolyl-, N-o-ethylphenyl-, and N-p-chlorophenylitaconimides were polymerized using the above procedure. Concentrations of the monomers, their conversions, and softening points of the polymers obtained are listed in Table 4.

In the case of the polymerization of N-phenyl and N-p-tolylitaconimides, four different concentrations of each monomer in THF were polymerized in order to find the optimum concentration. The results of these experiments are listed in Table 4.

Procedure for Anionic Polymerization of N-Arylitaconimides

In a two-necked 250 mL flask was placed 0.006 mol of the monomer dissolved in 50 mL of pure dry solvent such as THF or toluene.

TABLE 4. Monomer Concentrations, Percent Conversions, and Softening Points of the Produced Polymers from Free Radical Polymerization of Some N-Arylitaconimides

Run no.	Monomer	Concentration (g/100 mL THF)	% Conversion	Softening point of polymer (°C)
1	N-Phenylitaconimide	2.50	66	215-225
2	N-Phenylitaconimide	3.75	73.3	220-230
3	N-Phenylitaconimide	7.50	86.6	230-245
4	N-Phenylitaconimide	15.00	93.3	250-260
5	N-p-Methoxyphenylitaconimide	2.50	53.3	210-220
6	N-p-Methoxyphenylitaconimide	3.75	60.0	225-230
7	N-p-Methoxyphenylitaconimide	7.50	73.0	240-250
8	N-p-Methoxyphenylitaconimide	15.00	93.0	245-258
9	N-p-Tolylitaconimide	3.75	60.0	220-225
10	N-o-Ethylphenylitaconimide	7.50	66.6	220-230
11	N-p-Chlorophenylitaconimide	7.50	80.0	165-170

The contents were stirred with a magnetic bar under argon gas. The reaction mixture was cooled to -50°C before the injection of 0.5 mL of an ether solution of n-butyllithium as initiator in each case. The initiator concentration was thus equal to 0.102% by weight. Transfer of the initiator was accomplished in a glove bag under argon through a rubber sleeve stopper placed on the first neck using a hypodermic syringe. The second neck was connected to argon gas. The color of the solution changed immediately to red by the addition of the initiator. Stirring was continued for 5 to 10 min at -50°C . The red color was discharged by the addition of few drops of dilute hydrochloric acid before pouring it into 200 mL of methanol. A white precipitate was formed which was warmed, filtered, washed with methanol, and dried in a vacuum oven before weighing. Table 5 lists the conditions and results of the anionic polymerization of several N-arylitaconimides.

TABLE 5. Conditions and Results of Anionic Polymerization of Some N-Substituted Itaconimides^a

Monomer	Solvent	Concentration (g/100 mL)	T (°C)	% Conver- sion	Softening point of polymers
N-p-Methoxyphenyl- itaconimide	C ₆ H ₅ -CH ₃	3	25	Trace	-
			-50	20	-
	THF	2	-50	44	250-260
			-70	80	250-260
N-Phenylita- conimide	THF	2	-50	50	250-260
N-p-Chlorophenyl- litaconimide	THF	2	-50	00	-
N-p-Tolylitacon- imide	THF	2	-50	55	270-280
N-o-Ethylphenyl- itaconimide	THF	2	-50	5	Above 300

^aThe initiator was n-butyllithium, and its concentration was 0.102% by weight in each case.

RESULTS AND DISCUSSION

Monomer Synthesis

Although there are several procedures for the preparations of N-substituted cyclic imides [16-19], none of them was found suitable for the preparation of N-substituted itaconimides without modification. Almost all the available procedures involve heating of the intermediate amic acid produced from the reaction of the desired primary amine with the desired cyclic anhydride [16]. Heating of the amic acid may be performed alone or in the presence of a dehydrating agent as shown on the following page.

Dehydrating agents employed in this cyclization include acetic anhydride, acetyl chloride, phosphorous pentachloride, phosphorous trichloride, and thionyl chloride. Applying such methods to dehydrate

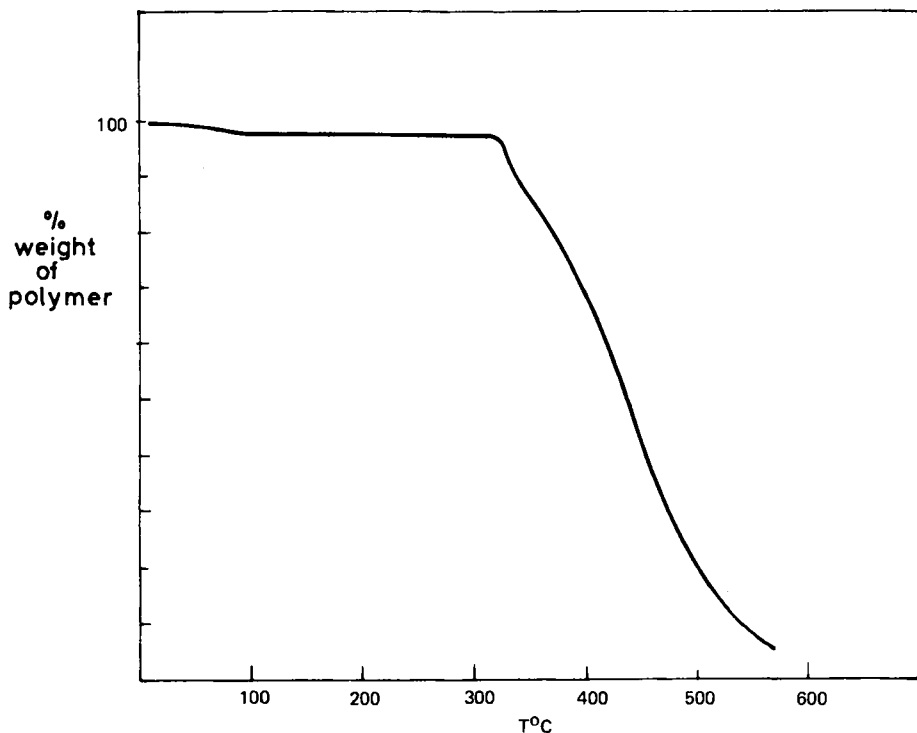


FIG. 1. Thermogravimetric analysis of poly(N-p-methoxyphenylitaconimide) prepared by radical polymerization.

were polymerized at similar conditions to find the optimum concentration. The results are listed in Table 4 and indicate an increase in conversion with an increase of monomer concentration. Furthermore, the softening points of the polymers obtained also increased with an increase of monomer concentration. The polymers produced were of low molecular weight as indicated by their low intrinsic viscosities [$\eta_{inh} = 0.026$ for poly(N-p-methoxyphenylitaconimide), prepared free radically] and from their high solubilities in a variety of solvents such as chloroform, methylene chloride, acetone, and THF. However, the polymers did not dissolve in methanol, ethanol, benzene, or cyclohexane. The formation of low molecular weight polymers was rationalized on the fact that each monomer contains two allylic hydrogens that can cause chain transfer reactions in addition to retarding the polymerization.

Poly(N-phenylitaconimide) exhibited rather high thermal stability when a sample of it was examined by a Thermal Gravimetric Analyzer. Decomposition and loss of weight started above 315°C. Such behavior is typical for polyimides [1] (see Fig. 1).

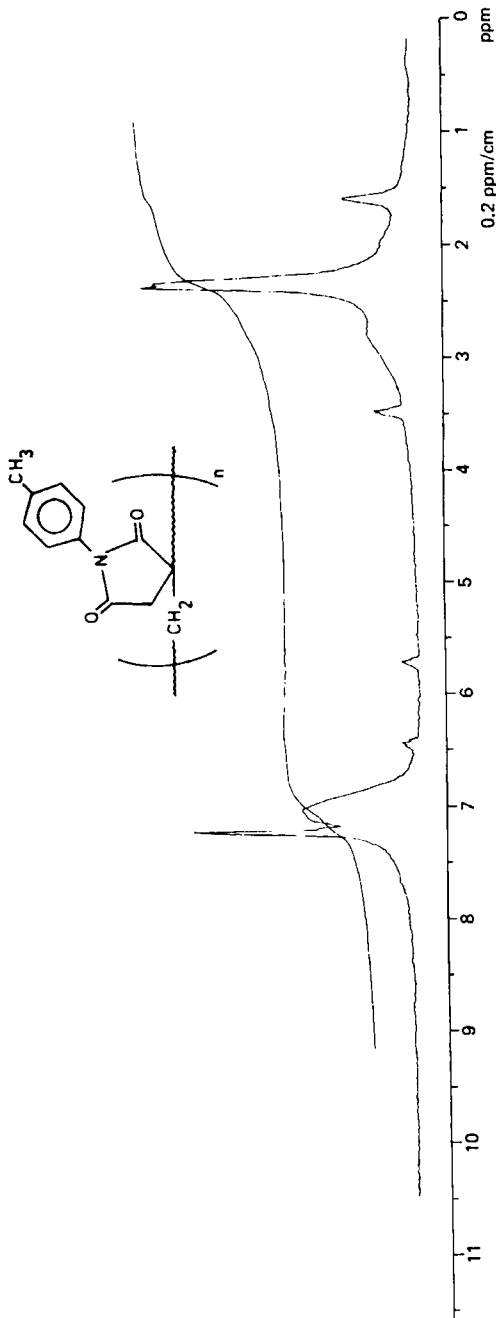
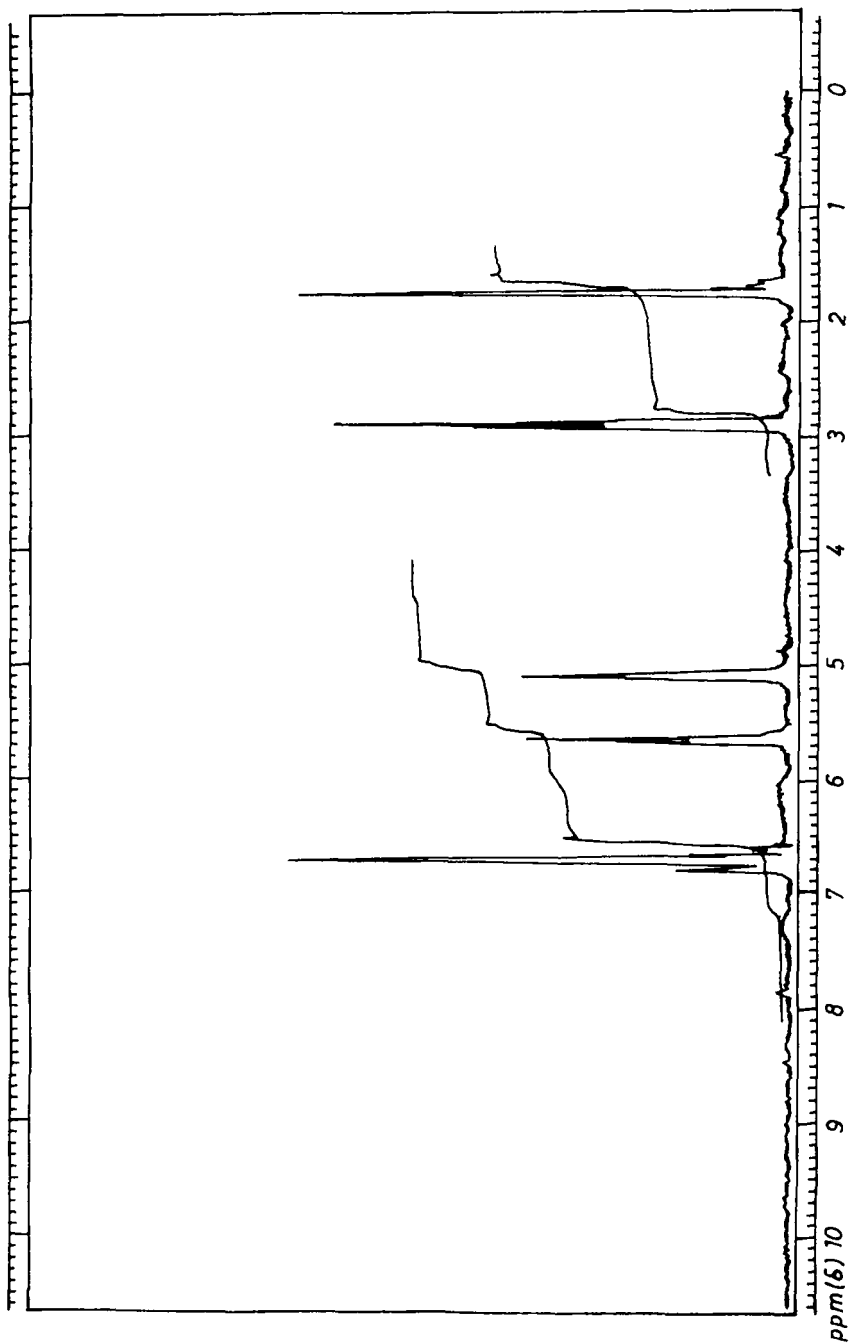
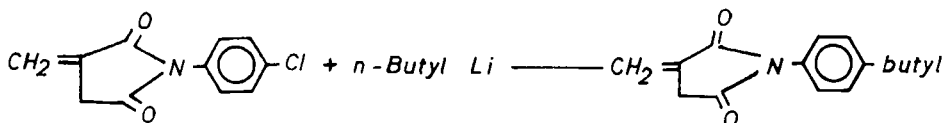


FIG. 2. NMR spectrum of poly(N-p-tolyl)itaconimide.

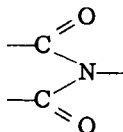
FIG. 3. NMR spectrum of N-p-tolylitaconimide in CDCl_3 .

Anionic Polymerization

Four of the monomers prepared were polymerized anionically using *n*-butyllithium as initiator and THF as solvent. When toluene was employed as a solvent, polymerization did not occur even at -50°C , indicating the high polarity of the propagating step. THF was a suitable solvent for such polymerization even at room temperatures. Yields and softening points of the polymers obtained by anionic polymerization are listed in Table 5. With the exception of *N*-*p*-chlorophenylitaconimide, all the monomers listed in Table 5 polymerized. *N*-*p*-Chlorophenylitaconimide did not produce any polymer even at -50°C . This may be attributed to the possibility of another reaction which may be the attack of the initiator on the benzene ring in a nucleophilic aromatic-type substitution replacing the chlorine:

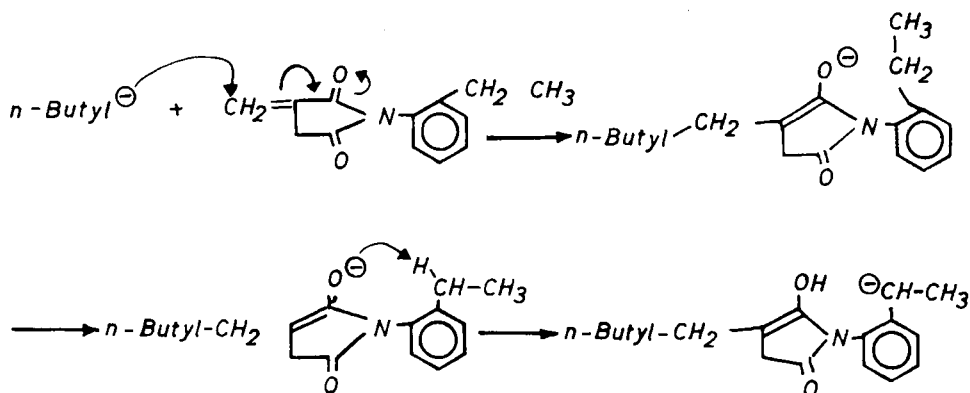


Such a substitution might be faster than addition of the initiator to the vinyl if we realized the strong electron-withdrawing ability of the imido group



N-*o*-Ethylphenylitaconimide produced a highly cross-linked polymer. Evidence of the network nature was the fact that the polymer was insoluble and infusible. It seems that the presence of two benzylic hydrogens in addition to two allylic ones may be responsible for such cross-linking. The two benzylic hydrogens of the ethyl group seem to be labile toward chain transfer reactions more than the paramethyl group hydrogens of *N*-*p*-tolylitaconimide which are also benzylics. This may be rationalized on the basis of the proximity of the methylene group to the carbonyl through which a six-membered ring intermediate facilitates a chain transfer reaction as indicated by the scheme on the following page.

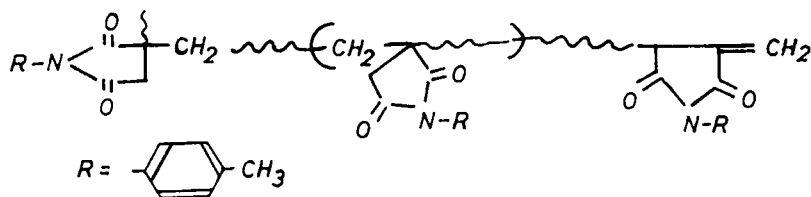
Such a chain transfer mechanism is not possible for *N*-*p*-tolylitaconimide. The NMR spectra of the polymers obtained by free radical or by anionic polymerization seemed to be similar in general. For example, the NMR spectrum (CDCl_3) of poly(*N*-*p*-tolylitaconimide)



showed residual vinylic protons centered at 6.10 delta which corresponded to the chemical shift of vinyl protons of N-p-tolylitaconimide. A new peak at 1.60 delta appeared in the NMR spectrum of the above polymer and was assigned to the methylene protons.

All the other poly(N-arylitacconimides) whose NMR spectra could be obtained revealed similar residual vinyl protons. The residual vinyls in the polymers were also evident in their IR spectra. The absorption peak around 1665 cm^{-1} did not disappear completely from the IR of the polymers.

Based on the above evidence, a partial structure for poly(N-p-tolylitaconimide) was proposed:



The NMR spectra of poly(N-p-tolylitaconimide) and of its monomer are presented in Figs. 2 and 3, respectively, for comparison.

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