

Chapter II

Literature Review

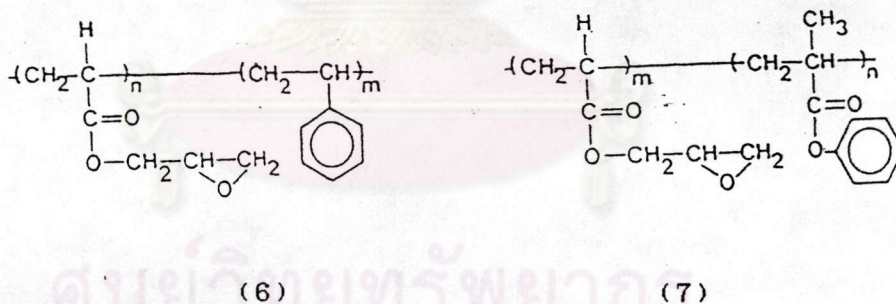
2.1 Literature Review of Negative Resists

Because of a high sensitivity of negative resists, much work on negative resists has been done. They could be classified into electron-beam, X-ray, and photosensitive resist due to the energy exposure.

2.1.1 Electron-beam Sensitive Negative Resists

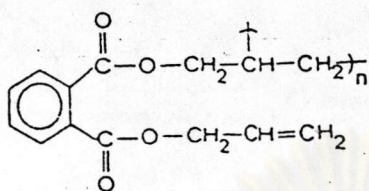
Though many classes of compounds were examined in the past as negative electron-beam resists [8], recent work was concentrated on three major categories : epoxy group containing polymers, polymers with pendant unsaturation, and vinyl aromatic polymers. It has generally been shown that in the epoxy group containing polymer class, the placement of epoxy group as side chains of the polymer, as opposed to in the backbone, results in marked improvement in the contrast of the resist. Nonogaki.S and et al [9] synthesized the epoxide containing polybutadiene by epoxidation of polybutadiene (1). They had high sensitivity, but low contrast (lower than 1). As a consequence of this, current efforts in this area are directed toward synthesizing and evaluating polymers prepared from glycidyl ester monomers. Hamermesh and Crane [10] attempted to prepare poly(ethylacrylate-co-glycidylmethylacrylate), which was known under the trade name "COP"(2). Thomson and co-worker

Feit et al [13] attempted to characterize the resist response of GMA homopolymer and copolymers with ethyl acrylate (EA). This has been successful features for 5 μm , and these parameters could be related to the molecular properties of the polymers. At lower feature sizes, however, other factors like solvent-induced swelling of images, wetting properties of developer and polymer and gel-rupture by forced development came into play. Thomson and co-workers [14] at Bell Laboratories examined copolymers of GMA and glycidylacrylate (GA) with styrene (6) and phenyl methacrylate (7) as negative electron resist materials. These copolymers had sufficient sensitivities for application and, in general, GA copolymers were more sensitive than the corresponding GMA copolymers. All these materials also showed better thermal stability than the GMA-GA copolymers.

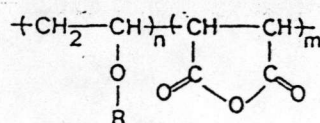


In the case of ethylenically unsaturated polymers, it has again been established that when the unsaturation is in the side chain of the polymer, the sensitivities of the resist are better than when they are in the backbone. One such polymer that has received wide spread attention is poly (diallyl-orthophthalate) (PDOP) (8), which is good thermal stability [15]. Recently, Yoneda et al [16] had optimized molecular weight and dispersity of this material for making

high-resolution patterns. Vertical wall profile with $1\ \mu\text{m}$ line widths were obtained with sensitivities of $4 \times 10^{-6}\ \text{C}/\text{cm}^2$ at 15 kV. This material showed acceptable fluorocarbon sputter etching resistance.



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Cole and his associates at General Electric Co. had reported [17] highly sensitive negative resists prepared as alkenyl half-ester from copolymer of vinyl ethers and maleic anhydride (9). Sensitivities in the order of $10^{-6}\ \text{C}/\text{cm}^2$ at 9kV were reached. The importance of the ether group was evident in these polymers, although their exact function had not yet been established. Despite their high sensitivity, the storage stabilities of these resists were quite good.

Vinyl aromatic polymers have been widely studied as negative electron resist. The simplest polymer of the rather large group is polystyrene and, although it has several disadvantages, it is one of the early candidates in electron-beam lithographic applications. It has excellent processing properties but has a very low sensitivity ($2 \times 10^{-4}\ \text{C}/\text{cm}^2$). Lai and Shepherd [18] had recently examined the effect of the molecular weight and its distribution on the performance of polystyrene as an electron resist. Their researches showed that the sensitivity increased with molecular weight and narrow dispersity gave improved contrast. Line widths $< 1.0\ \mu\text{m}$ had been

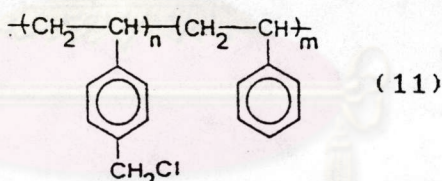
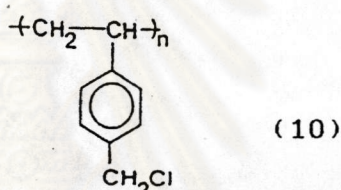
obtained with this negative resist. Sensitivities of 1×10^{-5} C/cm² had been reported, and very good plasma etching resistance had been observed.

The rather poor sensitivity of polystyrene and yet its good processibility and ready availability at a low price have prompted significant research in chemically improving its susceptibility to crosslink by electron-beam exposure. The strategy by which this problem is being commonly addressed is introducing electron-sensitive substituents into the phenyl rings. Halogenated of the phenyl rings has this effect, and the use of iodinated polystyrene for this propose has recently been described [19]. Researchers at Hitachi Ltd. had prepared iodinated polystyrene by direct iodination of polystyrene and found the sensitivity of the polymer to be increased through this process. The resist would not crosslink in a vacuum after exposure, indicating a short lifetime of the active species produced by the irradiation. It was ion-millable and showed good thermal stability.

Feit and Stillwagon [20] had prepared a chlorinated polystyrene with narrow molecular weight distribution and had observed that at 70 % chlorination, the material was 5.4 times more sensitive than polystyrene. As in the case of polystyrene, the contrast was very sensitive to the dispersity of the polymer and the latter is broadened by the chlorination process.

Imamura . S [21] studied chloromethylated polystyrene (CMPS) which prepared by chloromethylation of polystyrene. It

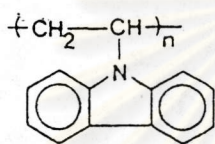
showed that the presence of a C-Cl bond (20 % by weight of chlorine) increased the sensitivity. As expected for negative resist, the sensitivity increased with increasing molecular weight, while the contrast increased with decreasing molecular weight distribution. The resolution observed was about 0.3 μm and the plasma etching resistance was 40 $\text{\AA}/\text{min}$. Recently, Choong H.S. thoroughly examined poly(chloromethylstyrene) (PCMS) (10), whose lithographic properties were better than those of CMPS. Also its copolymer with styrene (11) improved the contrast and etching resistance because of the presence of phenyl ring.



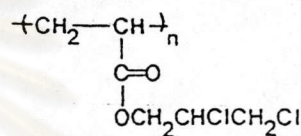
Other vinyl aromatic polymers had been examined by Jagt and Sevrien [22], e.g., poly(vinyl-carbazole) (PVK) (12) and poly(3-bromo-N-vinyl carbazole), like polystyrene (PS), had a high contrast and dry etching resistance properties, but the sensitivities were not sufficiently high unless molecular weights were very high. The bromo-derivative, however, has a much higher sensitivity (10^{-6} C/cm^2). Experiments also showed that the addition of organic bisazides, e.g., 4,4-diazidostilbene, to polystyrene or poly(vinylcarbazole) was

effective in increasing the sensitivity of these resists tenfold, with no loss of contrast.

Gazard et al [23] had synthesized a poly(methylmethacrylate)(PMMA) which was grafted with acrylic acid. It formed a negative system on development with solvents for PMMA. Sensitivities as high as 2.8×10^{-8} C/cm² at 20 kV have been reported for this process.



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2.1.2 X-ray Sensitive Negative Resist

Taylor et al [24] examined chlorine-containing acrylate homopolymers as resists for X-ray exposure at 3.5 mJ/cm² flux (1C/cm² at 1 kV = 10⁶ mJ/cm²). Highly sensitive materials, requiring less than a minute of exposure, had been found, but these showed rather low contrast, attributed to competitive intramolecular cross-linking reactions. Optimum properties were obtained for poly(2,3-dichloro-1-propylacrylate)(13), which also showed excellent stability. Lines and spaces of 1 μm could be obtained with sensitivity of 7 mJ/cm².

Several polyvinyl ethers have been reported as X-ray resists [25]. These polymers are prepared by the cationic polymerization method, and the exposures have been done at 5.4 Å.

The polymers with chlorine or vinyloxy group containing side chains gave good sensitivity ($>18 \text{ mJ/cm}^2$), while those with chlorine also showed good contrast (<2.2). The negative X-ray resists and their sensitivities were exhibited in Table 2.1

Table 2.1 Negative X-ray Resists

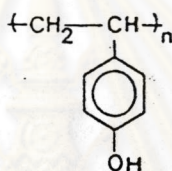
Polymer composition	Target wavelength, nm	Absorbing element	Sensitivity, mJ/cm^2
glycidyl methacrylate-ethyl acrylate (COP)	0.43 (Pd)		175
2,3-dichloropropyl acrylate (DCPA)	0.43 (Pd)	Cl	7.0
blend of COP and DCPA (DCOPA)	0.43 (Pd)	Cl	15.0
2,3-dibromopropyl acrylate-glycidyl methacrylate	0.46 (Rh)	Br	15.0
chloroethyl vinyl ether-ethyl vinyl ether	0.54 (Mo)	Cl	72
chloroethyl vinyl ether-vinyloxyethyl acrylate	0.54 (Mo)	Cl	18
chloromethylstyrene	0.43 (Pd)	Cl	25
allyl methacrylate-2-hydroxyethyl methacrylate	0.74 (W)		9

2.1.3 Photosensitive Negative Resists

Optical lithographic methods are most important for the manufacture of integrated circuits on a worldwide basis. The photoresists used are mainly sensitive in the wavelength from 300-500 nm. Some important research works could be reviewed as follows.

The photochemical reaction between polyvinyl alcohol (PVA) (14) and chromate species had been widely used in imaging devices. Steihler, Duncalf and Dunn [26] did some of

the early mechanistic work on this system and more recently Branin and Fonger [27] had examined the photochemical process. Nice and Farlee [28] have studied the chromate ion reaction with PVA in aqueous solutions by UV and electron paramagnetic resonance spectroscopy. It was found that during irradiation, the charge-transfer absorptions of the chromate esters initiated the photochemical reaction. The results were compared with those of the previous mechanistic studies made on this system. A proposed stepwise was a reduction of the Cr species to Cr (III), which finally complexed with PVA.



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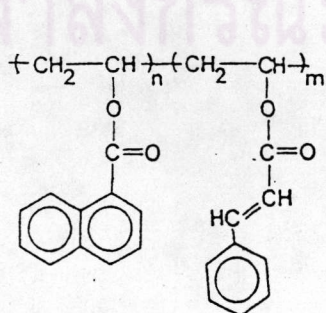
The sensitization of chromated PVA to visible laser wavelengths had been investigated by Bloom and Burle [29]. They found that compounds that were used for sensitization were sodium fluorescein, 2,4,6-tritolyprilium tetrafluoroborate, 2,4-dinitro-1-naphthol, and methyl orange.

Slobodkin and co-workers [30] had examined the relative merits of different drying and curing modes of PVA-dichromate compositions. Undesirable post-polymerization was found to appear to a large extent in infrared process.

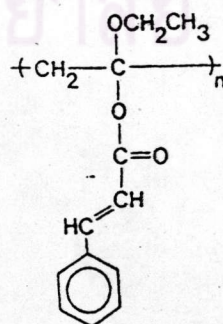
Several chemically modified derivatives of PVA had been developed recently to prepare negative photoresists. Thus, Daly and Engebrech [31] had prepared copolymers of vinyl

cinnamate with vinyl naphthoate or vinyl-3-naphthyl acrylate (15) by coesterifying PVA1 with the appropriate acid chlorides, giving acid-resistant photoresists. After UV exposure and development, the remaining crosslinked polymer could withstand hot nitric acid "deep etch" conditions.

Polyvinyl ethers with side chain unsaturation had been synthesized by Biryukova et al [32] by polymerization of the corresponding monomers with a cationic initiator like $\text{BF}_3 \cdot \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$. These polymers gave photochemical crosslinking with benzoquinone-Michler's lactone and, as photoresists, resolution of 1 μm line widths were obtained. Koto and Nakane [33] had recently described cationically polymerized 2-vinyloxyethyl cinnamates (16) as a negative photoresist with greater sensitivity than commercially available polyvinyl cinnamate resists, and about twice as much sensitivity as the rubber-based resists. Its resolution was comparable to photoresist under the trade name "AZ-1350", which was remarkable for a negative photoresist. The material was also reported to be excellent in terms of adhesion, thermal stability, and resistance to pin-hole formation.

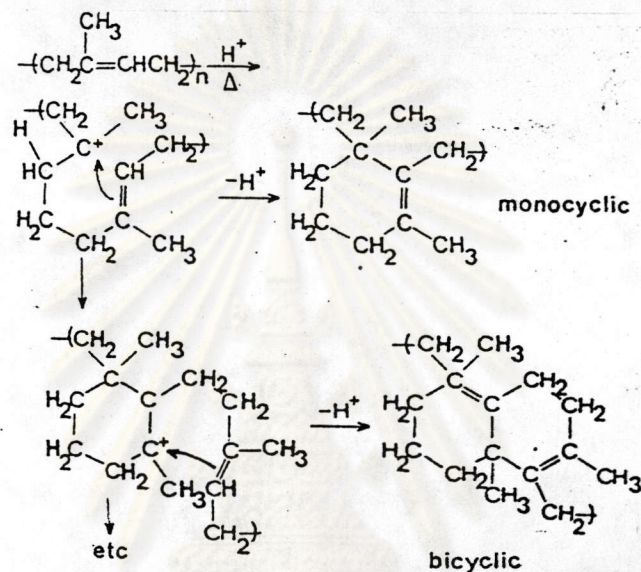


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Cyclized rubbers (Scheme 2.1) had been used extensively in the negative photoresist applications, and several commercial materials of this class were available, e.g., KMER, KTRF, Waycoat IC and SC, and Dynamic CMR and Micro-G. The most common composition in this family is a cyclized form of polyisoprene and photoactive crosslinker, typically a bisazide, which photolizes to the highly reactive dinitrene.



Scheme 2.1 Cyclization of polyisoprene

Treushnikov et al [34] had carried out theoretical and experimental studies to explain the important contributing factors that affected the photo-sensitivity of cyclorubber-bisazide system. It appeared from this work that, apart from more crosslink formations, parameters like the distribution of bisazide molecules in the film and the average number of the structural formation per polymer molecule capable of functioning as effective molecular network units were important. This research group had also examined [35] the effect of such factors as the method of solution preparation, solvent removal from cast film, storage time of prepared solution, and air versus vacuum exposure on the photo-sensitivity of cyclorubber-

2,6-bis(4-azidobenzal)cyclohexanone system, the changes in sensitivity of those materials which changes of drying temperatures might be attributed more to molecular conformation changes than to residual solvent. The effect of low-molecular-weight solvent in cyclized rubber and polystyrene coating on the mobility of the nitrenes formed by photolysis had also been studied [36]. Coating containing stable microvoids did not require solvents for nitrene mobility and those that absorbed wafer inhibited this mobility by such absorption. Treushnikov and co-workers [37] found that the negative photoresist FN-11 and a bisazide showed the interesting property of increased light sensitivity of the unexposed areas. This was explained theoretically and experimentally by an oxygen-pumping mechanisms from the dark parts to the exposed parts. Exposure in air gave much lower resolutions than in an inert atmosphere where the crosslinking reaction of dinitrene effectively competed with the much faster oxygen-nitrene reaction.

Shimizu and Bird [38] had contributed significantly to the understanding of the mechanism of photocuring of the cyclo-rubber bisazide-system. At 100 °C, the oxidative crosslinking by polymerization of the cycloisoprene was predominant over the thermal crosslinking produced by the bisazide. Significant crosslinking of the resin inhibited further bisazide decomposition by cage effect of the rigid matrix.

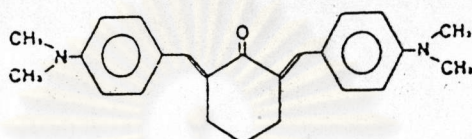
A 43 % quantum yield was established for the simultaneous cleavage of both the azide groups in the molecule of the bisazide, from the absorption of one photon of energy. The products of the azide decomposition were implicated in

inhibiting further bisazide decomposition by an energy transfer process. The chemical mechanism of crosslinking and reciprocity failure is evidenced by the appearance, on exposure, of a new absorption band at wavelength 410 nm. which was attributed to the bisamine crosslinking from comparison with the model compound, 2,6-bis(p-dimethylaminobenzal)cyclohexanone(17). The reciprocity effects were explained by competitive reactions of the nitrene with oxygen and polymer, the first being greater than 10^4 times faster than the latter. The sensitivity can be significantly enhanced by inert atmosphere or rapid exposure, both of which cause a low equilibrium oxygen content in the exposed areas. The azide-to-nitrene reaction is not affected by the oxygen content, but the consumption of the nitrene, once formed, can be decreased by minimizing the oxygen in the film.

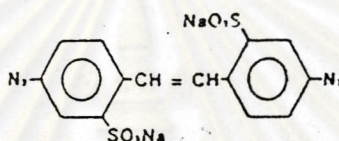
Cyclized cis-1,4-polybutadiene has also been developed into a photoresist. This resist showed a higher sensitivity than cyclized polyisoprene and had good resolution properties (1.6 μm). The polymer showed no resist flow up to 250 °C, and the decomposition temperature was higher than for polyisoprene. The polymer was prepared by cyclization of the monomer with organo-aluminum catalysts. The photoinitiator used was 2,6-bis (4-azidobenzal)cyclohexanone.

Naumova et al [39] had photocrosslinked an oligomeric 1,3-cyclohexadiene using 2,6-bis(4-azidobenzal)-4-methylcyclohexanone as a catalyst. Images of resolution 100-200 lines/mm had been successfully made with this material for photofabrication of optical screens and scales.

The bisazide system has been used to crosslink for non-rubber polymers to prepare negative photoresists in the recent past. Thus, Akagi et al [40] had used a formulation based on polyvinyl pyrrolidone, polyacrylamide, and 4,4-diazidostilbene-2,2-disulfonic acid disodium salt (18) to prepare a reciprocity-low-failing photoresist, the photosensitivity of which decreased rapidly with decrease in the light intensity.



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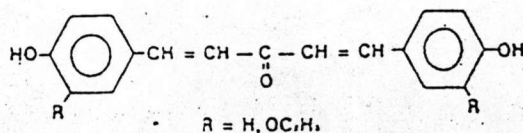


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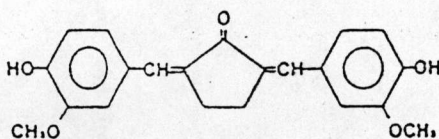


The mechanism involved generation of dinitrenes from the bisazide, which crosslinked the resin. As the light intensity was lower than the presence of oxygen, the dinitrene was effectively trapped. More oxygen therefore permeated into the layer and the crosslinking was further inhibited. This explained the reciprocity-low-failing characteristics of the material.

Some polyesters had been recently described in the area of photoresist. These polyesters contain unsaturated ketone moieties in the diol portion, e.g., substituted and unsubstituted. Bis(4-hydroxybenzylidene)acetone (19) and 2,5-bis(4-hydroxy-3-methoxy-benzylidene)cyclopentanone (20).



(19)



(20)

In the polyester derived from the latter, various metal atoms were incorporated by using metal dihalides to substitute partly the diacid chlorides in the solution condensation reaction.

The resulting polyesters were photosensitive and, coated on Al or Cu, could be exposed to UV-visible radiation and solvent developed to produce photoresists with 0.5-20 % of the image being the metal.

Stolyarova and co-workers [41] had observed that in ethylene propylene copolymers, bisazide photocrosslinkers caused increased sensitivity and contrast when exposures were carried out in an Ar atmosphere as opposed to that in air. From turbidimetric titration data, the best solvent for this copolymers was a 3:1 mixture of pentene-xylene.

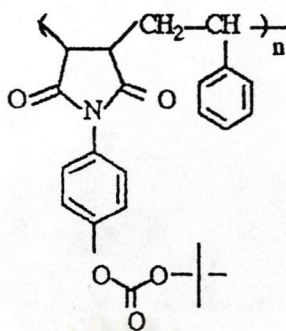
Crosslinking reaction through epoxy group ring opening has been demonstrated to be a feasible method of preparing negative resists, if the ring-opening reaction can be photochemically triggered using a latent inhibitor. Thus, glycidyl

methacrylate polymers were successfully crosslinked by photochemically generating PF_6^- from p-chlorobenzene diazonium fluorophosphate. The system sensitivity depended on the diazonium salt concentration, glycidyl methacrylate concentration, and the molecular weight of the comonomers.

2.2 Literature Review of N-substituted Maleimide Copolymers

Copolymers of N-substituted maleimides are mainly prepared to obtain new thermostable polymer materials. These polymers are characterized with high temperature of vitrifying. The interest on the polymaleimides grew also because of their unique properties as, e.g., physiological activity (antipyrene properties), optical and catalytic activity, etc. Based on these properties, copolymers of N-substituted maleimides are used also for preparation of membranes. Copolymerization of maleimide by free radical initiation has been studied extensively.

Richard Turner et al [42] had synthesized new, thermal stable resists, poly(styrene-co-N-(p-t-butyloxycarbonyloxy-phenyl) maleimide(21). These copolymers were prepared either by polymer modification or by copolymerization from monomers. Exposure of a resist formulated from the protected copolymers and a photoacid generator followed by baking results in efficient deprotection to produce the free phenolic copolymer in the exposed areas. The resulting latent image can be developed in either positive or negative tone upon proper choice of developers. The resulting relief images exhibit no detectable

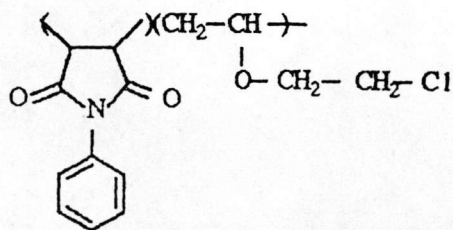
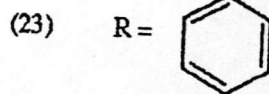
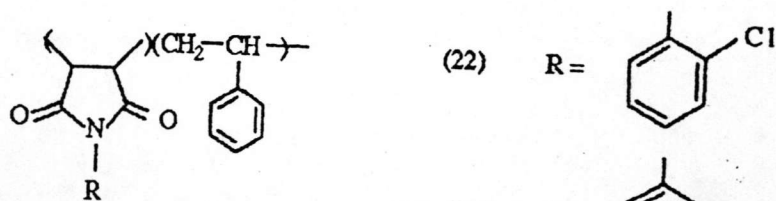


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change in size or shape after extended heating at 200 °C. From DSC analysis, the second heating of a polymer showed a T_g at 235 °C. Thermal gravimetric analysis of the t-BOC protected copolymers showed a precipitous loss of CO₂ and isobutene (25.4 % of sample mass) between 150 and 180 °C then a plateau followed by slow decomposition above 300 °C.

Mohamed A.A. and Jebrael F.H. [43] attempted to copolymerize styrene with (2-chlorophenyl)maleimides (22) by using AIBN as initiator. It has been shown that a charge-transfer complex participates in the process of copolymerization. The kinetic data of these systems were investigated, but thermal analysis was not studied.

Tirrel D.A. [44] had prepared poly(N-phenylmaleimide-co-styrene) (23) and poly(N-phenylmaleimide-co-2-chloroethyl vinyl ether) (24) by using reductive demercuration to generate the 1-butyl and benzyl radicals in mixtures of N-phenylmaleimide and either of the donor olefins styrene or 2-chlorophenyl vinyl ether. The mechanisms of these systems were investigated



and found that these copolymerization mechanisms differed from mechanistic schemes for radical polymerization in which 1:1 monomer complexes were added in a concerted manner to growing macroradicals. These copolymers had not been studied for thermal analysis data.

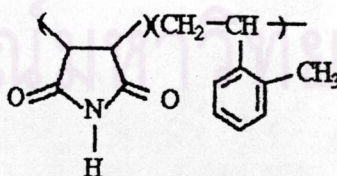
Otsu T. et al [45] attempted to synthesize poly(N-substituted maleimide) (Table 2.1) and investigated the effect of N-substituents on the radical polymerization by using AIBN as initiator in benzene.

Table 2.2 Radical polymerization of N-substituted maleimides in benzene at 50 °C for 5 hrs

RMI	R	Yield (%)	$(\eta_{sp}/c)^0$ (dL/g)	$\bar{M}_n^c \times 10^{-4}$	\bar{M}_w/\bar{M}_n
MI	H	34.3	0.29 ^{d)}	— ^{e)}	— ^{e)}
EMI	C ₂ H ₅	33.4	0.24 ^{d)}	2.1	2.3
IPMI	CH(CH ₃) ₂	74.0	0.58 ^{d)}	9.8	6.0
nSMI	{CH ₂ } ₃ CH ₃	78.4	0.76	15.9	2.6
IBMI	CH ₂ CH(CH ₃) ₂	66.6	0.50	6.9	3.0
sBMI	CH(CH ₃)CH ₂ CH ₃	70.9	0.53	9.5	2.5
tBMI	C(CH ₃) ₃	82.8	0.68	14.9	2.5
tAMI	C(CH ₃) ₂ CH ₂ CH ₃	71.2	0.61	13.0	2.1
CHMI	cyclo-C ₆ H ₁₁	39.1	0.27 ^{d)}	4.3	4.6
nOMI	{CH ₂ } ₇ CH ₃	40.1 ^{f)}	0.79	17.3	2.0
tOMI	C(CH ₃) ₂ CH ₂ C(CH ₃) ₃	26.5	0.27	5.0	1.8
DMI	{CH ₂ } ₁₁ CH ₃	46.5 ^{f)}	0.69	16.2	2.0
ODMI	{CH ₂ } ₁₇ CH ₃	44.6 ^{f)}	0.60 ^{g)}	17.0	2.0
BzMI	CH ₂ Ph	20.4	0.13	0.9	2.7
MBzMI	CH(CH ₃)Ph	47.5	0.30	7.4	2.0
DPhMI	CHPh ₂	20.4 ^{h)}	0.12	2.2	1.9
TrMI	CPh ₃	4.9 ⁱ⁾	—	6.3	1.3
PhMI	Ph	78.9	0.10 ^{d)}	— ^{e)}	— ^{e)}
2-MPhMI	2-(CH ₃)-Ph	27.6	0.17	3.3	1.9
2,6-DMPMI	2,6-(CH ₃) ₂ -Ph	20.4	0.10	1.9	1.6

The polymerization reactivities, % yield, and molecular weight of the polymers, were found to change depending on the structure of the N-substituents. From the thermogravimetric analysis showed that poly(N-cyclohexylmaleimide), poly(N-octadecylmaleimide), poly(N-phenylmaleimide), and poly(α -methylstyrene maleimide) had excellent thermal stability ($T_{\text{int}} > 360^\circ\text{C}$, $T_{\text{max}} \sim 430^\circ\text{C}$). The high thermal stability of these polymers were due to bulkiness of N-substituents.

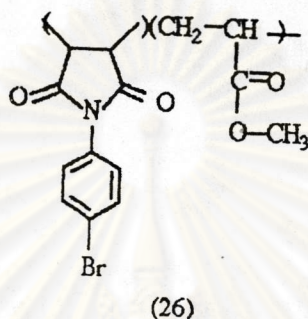
Ranogajec F. and co-workers [46] had prepared poly(α -methylstyrene-co-maleimide(25)). From the calorimetric curve it was observed that in the presence of an excess of maleimide, alternating copolymer was quantitatively formed prior to the formation of polymaleimide. Glass transition temperatures (T_g) of polymers were investigated by using differential scanning calorimeter (DSC). It was revealed that T_g of the alternating copolymer and polymaleimide blended with 80 % and 56.2 % of alternating copolymer were 567 °K (314°C), 580 °K (307 °C) and 587 °K (314°C), respectively, while polymaleimide decomposes on heating above 600 °K without any indication of T_g .



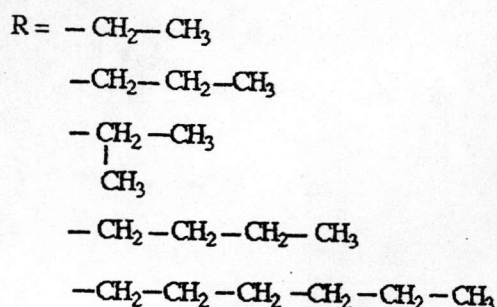
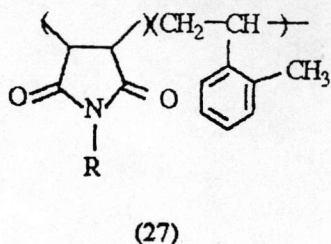
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Borbely J. and co-workers [47] performed radical polymerization of methyl methacrylate and N-(4-bromophenyl)

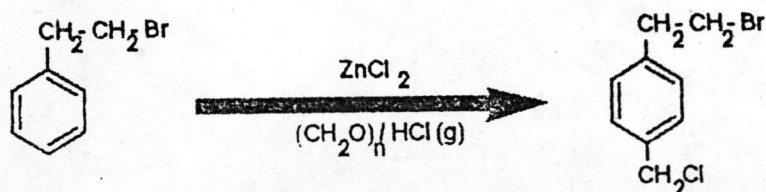
maleimide (26) in dioxane at 60 °C with AIBN as initiator. The glass transition temperature of copolymers with various composition were measured. A linear correlation was found between the T_g values and N-(4-bromophenyl)maleimide content. The T_g values were in the range of 108.5-209.6 °C.



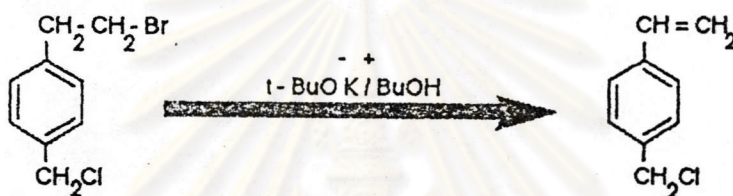
Ranogajec F. et al [48] had prepared alternating copolymers of α -methylstyrene with N-alkylmaleimides (RMI; R = Et; *n*-Pr; *iso*-Pr; *n*-Bu; *n*-Hex) (27) at different monomer-to-monomer ratios in the feeds using AIBN as initiator. The kinetic data and mechanisms were studied. It was found that the glass transition temperature (T_g) of poly(α -MeSt-alt-RMI) decreased when higher alkyl chain was introduced : R, T_g / °K : Et, 462; *n*-Pr, 454; *n*-Bu, 416; *n*-Hex, 382. The alternating copolymers of α -methylstyrene with N-(*iso*-propyl)maleimide had the highest T_g = 485 °K.



2. Chloromethylation of 2-phenylethyl bromide

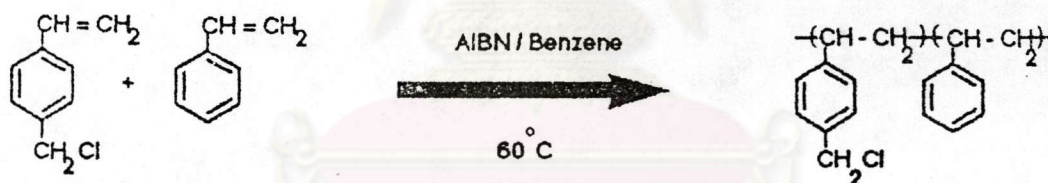


3. Dehydrobromination of p-(2-bromoethyl)benzyl chloride



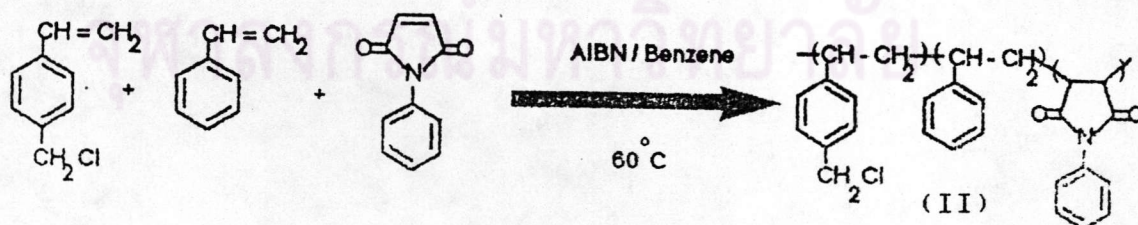
4. Polymerization :

4.1 Copolymerization of poly(p-chloromethylstyrene-co-styrene)



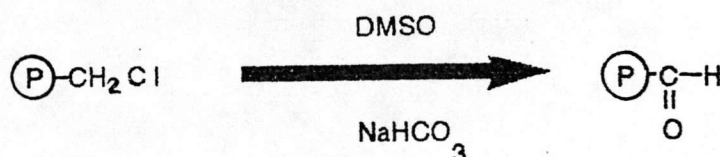
(I)

4.2 Copolymerization of poly(p-chloromethylstyrene-co-styrene-co-N-phenylmaleimide)

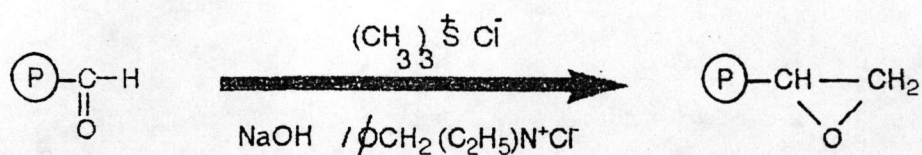


(II)

5. Carboxylation of chloromethyl groups

(Let (I) and (II) = $\text{P}-\text{CH}_2\text{Cl}$)

6. Epoxidation of carboxaldehyde groups.



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