



Research work of radiation induced graft polymerization to synthesis
and modification of polymer materials in CRICI

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Rising of the method in radiation induced graft polymerization as an independent field of polymer chemistry is tightly connected with intensive development of nuclear energetic and accelerator technology in the end 50th and beginning of 60th years. Rapid growth of new functional polymer technology, which is interested in our and foreign country, is stimulating continuous growth of RGP-an effective and universal method for synthesis and modification of functional polymer materials.

The direct and post radiation induced graft polymerization had been studied in CRICI. The method consists of irradiation of various polymer substrates in the presence (or absence) of monomers. The later being in a liquid, saturated vapour or gaseous and non-saturated vapour.

Our institute started to research radiation induced graft polymerization since the beginning of 60th years. Table 1 shows the research work of radiation graft polymerization, which had been studied more detail in CRICI.

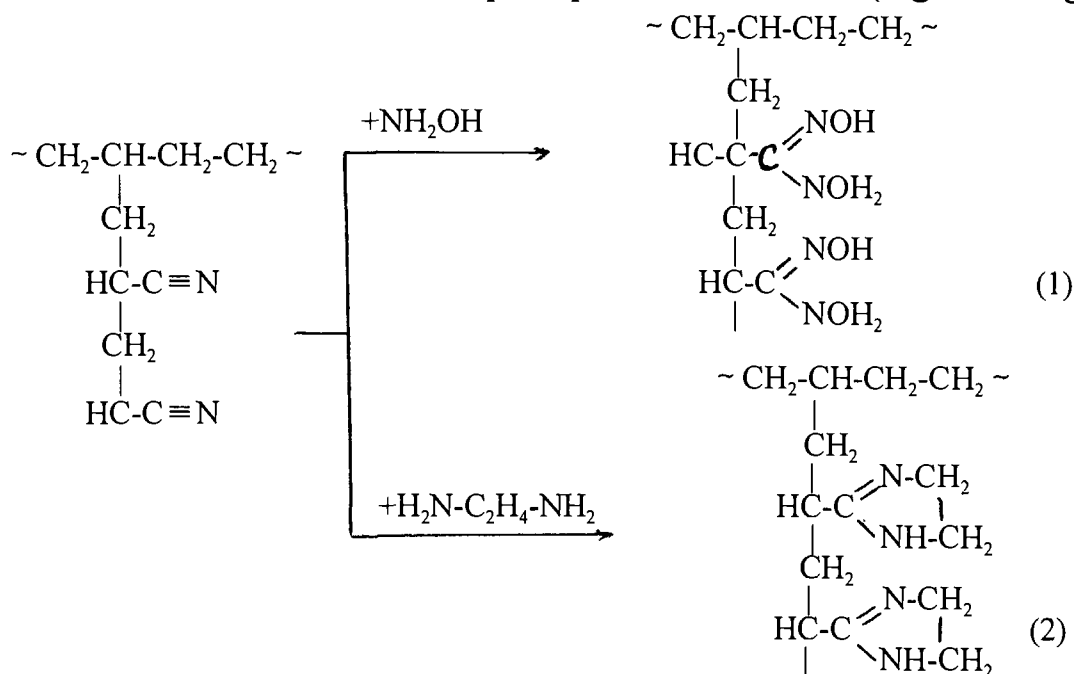
The more interesting is the following subjects of RGP, which will be discussed here.

1. Grafting of functional monomers. --- It is possible to divide the grafting into two main approaches for synthesis of functional polymer materials. The first is

grafting of monomers attached required functional group such as unsaturated carboxylic acid (acrylic and methacrylic acid), unsaturated nitrogen containing (alkali) base (vinylpyridine), monomers with hydrophilic unionized and polar groups (acrylamide, N-vinylpyrrolidone glycidylmethacrylate) and so on. The secondary is grafting of monomers capable of continuing chemical modification after graft polymerization. This approach essentially expands synthetic possibility of RGP for preparing functional polymers. It is due to the following reasons: On the one hand it is allowed to use the monomers, which are more convenient for graft polymerization onto the polymer substrates. After grafting the grafted polymer can further be modified to obtain grafted polymer with required functional groups. On the another hand some functional monomers are very difficult to graft onto the substrates, so some precursor monomers must be chosen in order to obtain desirable functional polymer materials. In this case it is worth to mention that the monomer of styrene is more popular to graft onto the majority of the practically important polymer substrates. Grafted chain of PSt is enable to suffer chemical reaction as analogical PSt homopolymer. One of these is sulfonation of grafted PSt chain in benzene cycle. We use this reaction for preparing ionexchange membranes in our laboratory. Another example is the monomer of acrylonitrile, which is very easily grafted onto polymer substrate. After grafting the grafted polyacrylonitrile chain can be reacted with a lot of chemical reagents. We had studied the radiation graft polymerization of acrylonitrile onto polyethylene film. After grafting the polyacrylonitrile was reacted with alkali and acid respectively and the hydrophilic polymer membranes of PAc/PE and PAAm/PE were obtained respectively.

More interesting is the preparation of membranes for pervaporation of

ethanol. That is, grafted polyacrylonitrile chain was continued to react with hydroxyamine and ethylenediamine respectively: Thus obtained functional polymer membranes can be used as pervaporation of ethanol (Fig.1 and Fig.2).



2. The effect of some salts on aqueous solution graft polymerization.

The grafting of AA or AAm onto PE by direct or post radiation method in the presence of Mohr's salt or cupric nitrate was studied in detail. It is well known that it is very difficult to perform effective graft polymerization of AA or AAm without mentioned salts, because of strong homopolymerization of monomers. The dependence of the grafting rate and concentration of salt is of great importance (Fig.3). We can see, at first the grafting rate increases because of more active suppression of homopolymerization as compared with graft polymerization. This fact can be explained since the concentration of salt in aqueous solution is higher than in the graft layer. This difference in concentration may be explained by the fact that the Fe^{+++} or Cu^{++} ions, whose

diffusions are difficult in the graft layer. When the concentration of salts is increased, the process of inhibition of graft polymerization increased as well.

3. Radiation induced graft polymerization by gaseous phase of monomers.

The direct or post radiation graft polymerization by gaseous phase of monomers onto polymer substrates had been studied in CRICI. This method consists of irradiation or preirradiation of various polymer substrates in the presence (or absence for preirradiation) of monomer. The later being in a gaseous of nonsaturated vapour state. Under the conditions of grafting in the gaseous phase the radiation energy is practically absorbed only by polymer substrate (specially for the condition of preirradiation) therefore the active centres initiating graft polymerization are mainly formed in the polymer substrate. As a result of this fact any undesirable processes of homopolymerization will occur to a very small extent. This approach of grafting may decrease the unnecessary expenditure of the monomer and in a number of cases it allows the elimination of additional processing or treatment of grafted materials by solvents.

As we know when the preirradiation of polymer substrate under air atmosphere the peroxide as the active centre is formed in polymer substrate. The example is grafting of gaseous or unsaturated acrylic acid onto preirradiated polyethylene.

We also had studied preirradiation of polytetrafluoroethylene and its copolymer with vinylidene fluoride under vacuum atmosphere. After irradiation the grafting polymerization was carried out with gaseous acrylic acid or styrene under reduced pressure. The amount of formed free radicals in the PTFE had been measured by ESR (Tab.2). Both the Tab.2 and Fig.4 show that the amount

of radical increases with increasing of dose and the degree of grafting increases with increasing of preirradiation dose.

The Fig.5 shows the comparison between two adhesive strengths. The curve 1 is the adhesive strength of acrylic acid grafted PTFE by method of post gaseous grafting polymerization and the curve 2 is the strength by liquid phase direct grafting polymerization.

The method of gaseous grafting polymerization is also effective for preparation of ionexchange membranes. The properties of styrene sulfonated ion-exchange membrane prepared from gaseous grafting polymerization of styrene onto PTFE are showed in Tab.3.

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Tab. 1 Some research works of radiation induced graft polymerization studied in CRICI

No	Polmer substrate	Graft monomer	Irradiation method	Graft system	Possibility of use
1	polypropylene	vinylpyrigine	direct	liq. phase	enhanced dyeability
2	Polyethylene	acrylic acid methacrylic acid	Direct	liq. phase +Fe ⁺⁺⁺	separating membrane for Ag-Zn cell
3	Polyethylene	HEMA	Direct	liq. phase	for medical use
4	PVDF	styrene → sulfonation	Direct	liq. phase	separating membrane for fuel cell
5	PTFE	acrylic acid styrene	direct direct	liq. phase +Fe ⁺⁺⁺	enhanced adhesiveness
6	NBR rubber	tetrafluoro-ethylene	direct	gas. phase	reduced friction coefficient
7	silicon rubber	NVP	direct	liq. phase	contact lense
8	silicon rubber	HEMA acrylic acid	direct	liq. phase +Cu ⁺⁺	intrauterine device (IUD) for birth control
9	PVC floor	acrylic acid styrene	direct	liq. phase	antistatic electricity
10	polyethylene	acrylonitrile → vinyl amidoxime vinylimidozoline	direct	liq. phase	membrane for pervaporation
11	SAN (styrene-acrylonitrile copolymer)	GMA(glycidyl methacrylate)	direct	liq. phase	compatibilizer for PA6/ABS alloy
12	Polyethylene	DMAEMA*	direct	liq. phase	antithrombosis
13	PTFE	acrylic acid styrene	post	gaseous phase	ionexchange membrane, enhanced adhesiveness
14	carbon fiber carbon black	acrylic acid	direct post	gaseous phase	improved compatibility with resin

DMAEMA*— — dimethylamineethylmethacrylate

Tab. 2 The Amount of Radicals vs Dose

Sample	1	2	3	4	5
Dose KGY	9.05	26.1	47.5	71.3	92.7
$N(\cdot 10^{-17})$	3.387	6.358	9.196	14.84	22.98

Tab. 3 The Properties of Ion-exchange Membrane

Sample	G %	Ion-exchange capacity(mmol/g)
A	12.5	0.1907
B	31.1	1.3259
C	40.5	1.9304
D	45.7	2.0136

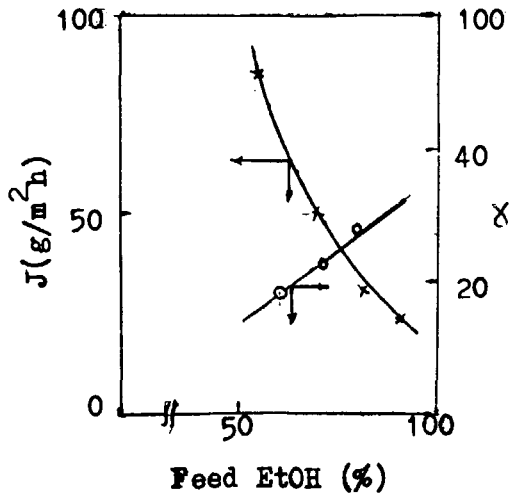


Fig.1 Pervaporation data of membranes containing amidoxime

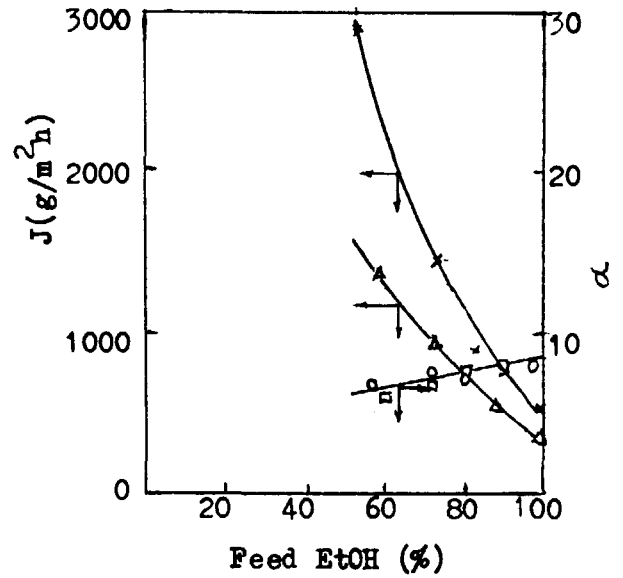


Fig.2 Pervaporation data of membranes containing imidazoline
 (x, o) High imidazoline content (Graft degree of AN: 120%)
 (Δ, □) Low imidazoline content (Graft degree of AN: 58%)

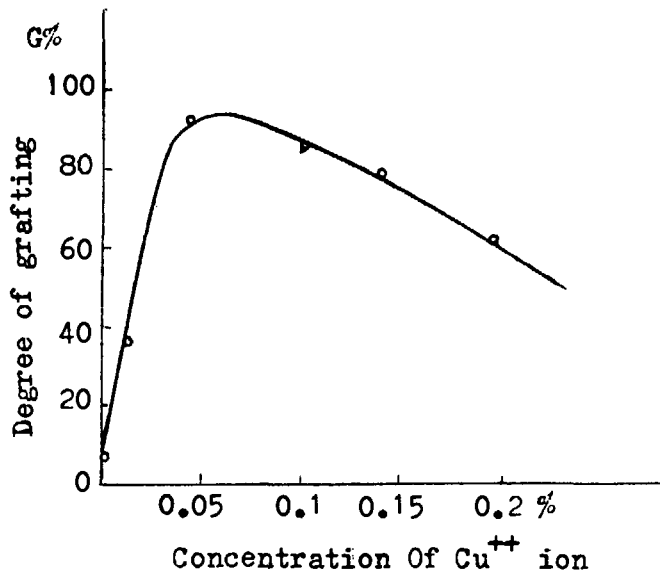


Fig.3 The dependence of grafting rate and concentration of Cu^{++} ion

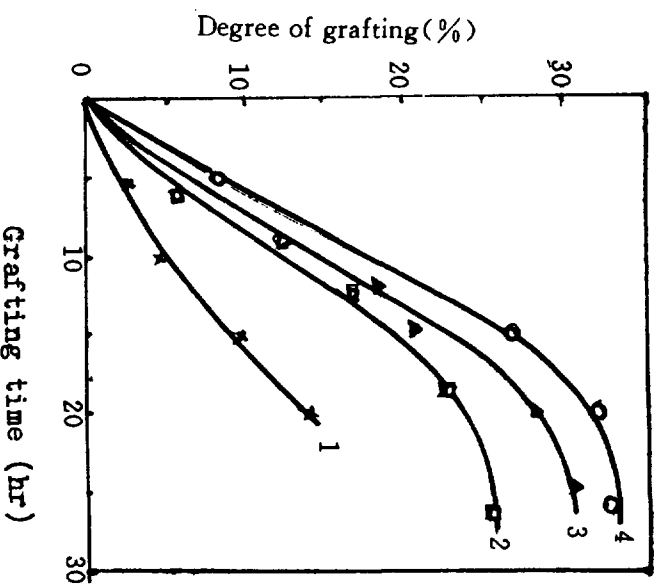


Fig. 4 Graft yield vs. time at various preirradiation doses. (1. 10KGy; 2. 12KGy; 3. 27KGy; 4. 48KGy) Grafting temp. 50C; Film thickness 0.10mm; Dose rate 1.32KGy/sec.

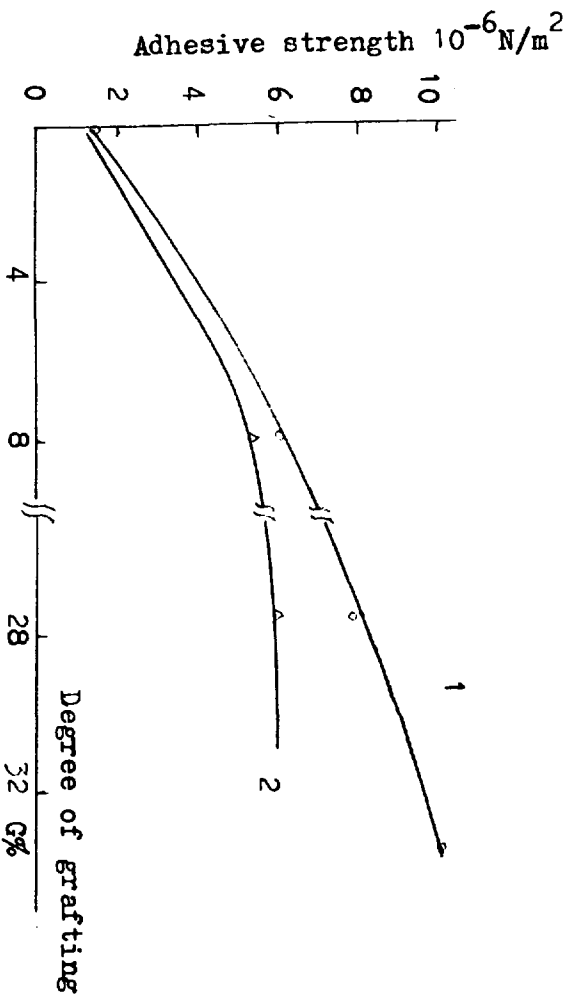


Fig.5 Comparison between adhesive strengths of two grafted PTFE prepared from gaseous & liquid phase methods respectively