Surface Photograft Polymerization of Vinyl Acetate on Low Density Polyethylene Film. Effects of Solvent

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ABSTRACT: To photograft vinyl acetate (VAc) onto low density polyethylene (LDPE) film, suitable solvents should be determined in advance. Different reagents were used as solvents of VAc (acetone, benzene, carbon tetrachloride, cyclohexane, cyclohexanone, ethyl acetate, methanol, tetrahydrofuran (THF) and N, N-dimethylformamide(DMF). All graft polymerizations were completed by two-steps, *i.e.*, benzophenone (BP) pre-coated film samples were prepared onto which VAc was grafted. To prepare film samples containing BP, BP should be dissolved in a suitable solvent. The effects of various solvents of BP on grafting were examined, including acetone, benzene, chloroform, 2,4-dioxane, DMF, ethyl acetate, n-hexane, methanol and THF. Percent conversion (CP), grafting efficiency (GE) and grafting percent (GP) determined by gravimetry and contact angles of grafted films against water showed that reagents have different effects on the graft polymerizations. Acetone is the most suitable as solvent of BP or VAc. The behavior of solvents seems closely related to the affinity with the substrate.
KEY WORDS   Photograft Polymerization / Low Density Polyethylene Film / Vinyl Acetate / Benzophenone / Solvent /

In our previous papers,[1,2] VAc was photografted onto LDPE film with different photoinitiators, and graft polymerization was verified with FT-IR spectra. Among photoinitiators, BP is preferred. The main grafting mechanism can be briefly outlined here. When irradiated with UV radiation, BP absorbs energy and is excited to singlet state [BP]^S and then relaxes to more stable triplet state [BP]^T. [BP]^T abstracts hydrogens from the chains of LDPE, leading to LDPE macromolecular free radicals generated. Adding monomer makes graft polymerization take place. BP pre-coating is the most suitable.[3] To prepare BP pre-coated film samples, BP should be dissolved in a suitable solvent. Reagents having different solubility parameters (SP) may show different diffusion behavior on film. Therefore, it is important to determine suitable solvents of BP. However, no studies have focused on this in the literatures. Some papers study the effects of solvents of monomer on graft polymerization.[4–6] From these studies, it is clear that affinity between substrates and monomers is a decisive factor for effective grafting. Swelling of the film caused by the solvents also has great influence on the distribution and average molecular weights of grafted chains.

The present paper centers on the effects of various solvents of BP and VAc on the photograft polymerization. Emphasis is laid on the solubility parameters of solvents to explain their behaviors.

EXPERIMENTAL

Materials

Monomer: Vinyl acetate (VAc, AR grade, Bp: 72—73 ℃, from Tianjin Tiantai Chemical Reagent Plant, China), was purified by distillation before use.

Photoinitiator: Benzophenone (BP, chemically pure grade, mp: 47—49℃, from Shanghai Reagent Plant No.1, China), was used as received.

LDPE film: Commercial LDPE film (63 μm in thickness, transparency to UV light, 75%, $\lambda = 254$ nm), was cut into circular samples with diameter of 70 mm, and subjected to Soxhlet extraction with acetone for 5 h to remove additives and impurities.

Solvent: Acetone, benzene, carbontetrachloride, chloroform, cyclohexane, cyclohexanone, N, N-dimethylform amide (DMF), 2, 4-dioxane, ethyl acetate, n-hexane, methanol, and tetrahydrofuran (THF), all analytically pure grade, were used without further purification.

Preparing BP Pre-Coated Films

BP pre-coated film samples were prepared as described earlier.[3] A drop of acetone (unless otherwise noted) solution containing a known amount of BP was placed between two film samples with a micro-syringe. A certain pressure was exerted to make the solution thin and even. The samples were separated and dried at ambient temperature and BP pre-coated film samples were obtained. The amount of BP on each sample was controlled by the volume of BP solution.

Grafting Procedure

The equipment for photografting and assembly of film samples for polymerization were introduced in detail in the previous papers.[1,2] A certain amount of monomer solution (pre-purged with nitrogen gas to exclude oxygen dissolved in the solution) was placed between two films with a micro-syringe. A appropriate pressure was given to make the reaction liquid thin and even. The system was covered with a piece of quartz plate, laid on the holder of the irradiation equipment at a distance about 15 cm from the UV lamp, and irradiated by UV radiation (UV lamp: high-pressure mercury lamp, 1000 w) at a given temperature controlled by a thermocouple thermometer. Polymerization was decided by a predetermined period of irradiation time.

When effects of solvents of BP on grafting were investigated, different solvents containing the equal amount

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of BP were used to prepare BP pre-coated film samples as substrates. Neat VAc was used as monomer. When effects of the solvents of VAc on grafting were studied, acetone solution containing given amount of BP was used to prepare BP pre-coated film samples. The samples were used as substrates and solutions of VAc (5 mol L^{-1}) in different solvents were used as monomer solutions.

After grafting, the samples were dried to constant weight and subjected to Soxhlet extraction with suitable solvents for 8 h to remove the homopolymer. Three grafting parameters, percent conversion (CP), grafting efficiency (GE) and grafting percent (GP) were calculated as follows:

$$CP = \frac{W_P}{W_M} \times 100\%$$

$$GE = \frac{W_G}{W_P} \times 100\%$$

$$GP = \frac{W_P}{W_F} \times 100\%$$

Where W_M is weight of monomer between the two films; W_P is weight of polymer formed, including homopolymer and grafted polymer, obtained by weighing the films after vaporizing residual monomer; W_G is weight of the grafted polymer, obtained after extracting the homopolymer with acetone; and W_F is the weight of LDPE film before grafting.

Alcoholysis and Measuring Contact Angles

By alcoholysis as reported earlier,[2] PE-g-PVAc was turned into PE-g-PVA. Contact angles of PE-g-PVA film samples against water were measured, as described in another paper.[2]

RESULTS AND DISCUSSION

Different Solvents of BP

Various reagents were applied as solvents of BP including acetone, methanol, ethyl acetate, dioxane, chloroform, n-hexane, THF, DMF and benzene, whose effects on graft polymerizaton of VAc are presented in Table I.

Nine reagents with different behavior, which may be related closely to solubility parameters (SP) listed in Table II, were used.

Generally, if SP of one reagent is closer to that of PE, it is easier for the reagent to diffuse through PE film. Chloroform, though its SP is around 9.4, has behavior similar to that of n-hexane. Methanol, whose SP is about 14.8, diffuses on PE films much more smoothly than DMF (SP = 12.0). According to SPs and behavior, the reagents are grouped as having higher affinity with PE film samples, such as n-hexane and chloroform; having medium affinity, including acetone, methanol, dioxane, ethyl acetate, THF and benzene; and having lower affinity, e.g., DMF. Mainly owing to different affinities, the results in Table I were obtained. Their behavior is illustrated in the following Figures 1A—1C.

n-Hexane and chloroform (Figure 1A) as solvents of

Table I. Effects of solvents of BP on polymerization

Solvent	BP/VAc/wt%	CP/%	GE/%	GP/%	Contact angle[a,b] degree
n-Hexane	1	9.3	2.0	0.05	91
n-Hexane	3	18.7	10.1	0.11	80
n-Hexane	5	28.0	28.3	0.45	75
Chloroform	1	14.9	1.1	0.05	92
Chloroform	3	24.3	7.6	0.11	85
Chloroform	5	29.9	28.1	0.48	78
Acetone	1	22.4	16.7	0.21	81
Acetone	3	46.7	46.3	1.23	72
Acetone	5	59.8	80.4	2.74	56
Methanol	1	20.8	13.5	0.16	79
Methanol	3	36.4	44.5	0.92	71
Methanol	5	59.2	62.5	2.11	65
Dioxane	1	19.6	12.8	0.14	80
Dioxane	3	37.4	32.5	0.69	76
Dioxane	5	53.5	59.0	1.80	64
Ethyl acetate	1	28.9	17.5	0.29	80
Ethyl acetate	3	35.5	50.0	1.01	72
Ethyl acetate	5	52.1	71.8	2.13	60
THF	1	19.6	8.1	0.09	82
THF	3	31.5	28.6	0.51	73
THF	5	51.8	57.5	1.70	66
Benzene	1	15.9	10.0	0.15	85
Benzene	3	31.5	50.1	0.90	73
Benzene	5	55.2	61.5	1.93	63
DMF	1	24.3	1.1	0.01	92
DMF	3	29.9	25.6	0.40	72
DMF	5	36.4	32.8	0.62	61

[a] Contact angle of PE film with water before grafting at 94°.
[b] Contact angle of inner side of sample; polymerization conditions: volume of VAc, 25 μL; intensity of UV radiation, 5010 μw cm^{-2}; temperature, 30℃; polymerization time, 4 min.

Table II. Solubility parameters of reagents [7]

Reagent	Solubility parameter(SP)
n-Hexane	7.2
LDPE [a]	7.9
Cyclohexane	8.18
Carbon tetrachloride	8.6
Vinyl acetate(VAc)	9.0
Ethyl acetate	9.1
Benzene	9.15
THF	9.2
Chloroform	9.4
Acetone	9.8
2,4-Dioxane	10.1
DMF	12.0
Methanol	14.8

[a] Low density polyethylene.

BP, they penetrate PE films rapidly, carrying BP molecules. When VAc is added, VAc cannot penetrate PE films at the same velocity as n-hexane and chloroform. Therefore, VAc and BP cannot contact effectively.

For acetone, methanol, THF, dioxane, ethyl acetate and benzene (Figure 1B), affinity with PE film is the same as that of VAc. So VAc molecules contact with BP molecules effectively. Polymerization of these systems thus proceeds smoothly.

The affinity of DMF with PE film is lowest (Figure 1C). When deposited between the two films, DMF concentrates mostly on the inner surface (F1 and F2, in Figure 2). When VAc is deposited, VAc carries BP along to the deeper layers of the film, making them sufficiently contact. Polymerization proceeds more smoothly than that of the system using n-hexane and chloroform as the solvents of BP, but less smoothly than those applying
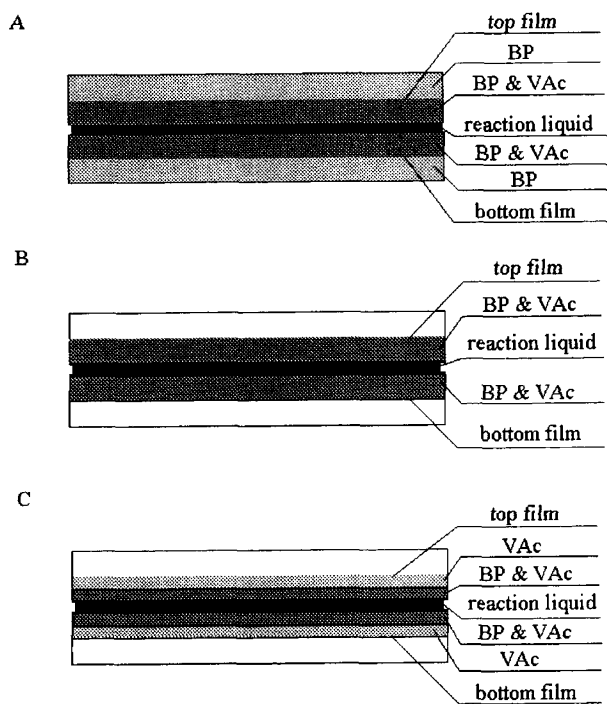
A

B

C

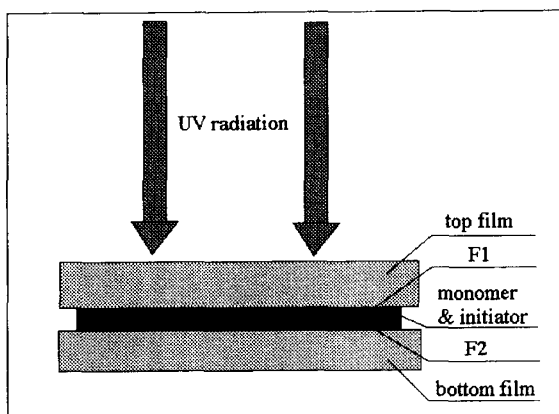**Figure 1.** Effects of affinity of the solvents with PE films on grafting polymerization.

Figure 2. Cross section of grafting polymerization.

acetone.

The data in Table I demonstrate that contact angles of the grafted films with water decline with increase of GP, irrespective of solvent. The explanation above can be verified indirectly to some extent by contact angles of grafted PE films (Table I). For the first group of solvents, contact angles decrease slowly, probably due to the low quantity of GP and deep penetration of the grafted chains. Regarding the third group, although all CP, GE, and GP of the polymerization systems are at a lower level compared with those of the second group, contact angles fall rapidly, indicating graft polymerization mostly takes place near the surface layer. For the second group, due to total effects of much more VAc grafted and more grafted PVAc chains diffusing on the surface regions of the film, the drop in contact angles is more considerable. Contact angles are influenced by several factors. From the above, solvent of BP acts just as a carrier, diffusing BP on the film. If the affinity between the sol-

Table III. Effects of solvents of VAc on polymerization

Solvent	Irradiation time/min	CP/%	GE/%	GP/%	Contact angle[a,b] degree
Acetone	1	25.8	26.7	0.18	80
Acetone	3	45.3	50.1	0.59	71
Acetone	5	69.8	79.9	1.46	63
Cyclohexanone	1	25.5	25.0	0.17	81
Cyclohexanone	3	37.8	34.2	0.33	75
Cyclohexanone	5	41.1	65.1	0.70	71
Methanol	1	26.7	26.7	0.19	78
Methanol	3	48.8	58.8	0.75	73
Methanol	5	54.7	64.7	0.93	65
Ethyl acetate	1	22.8	37.5	0.22	80
Ethyl acetate	3	45.5	50.0	0.60	70
Ethyl acetate	5	56.4	63.3	0.94	63
Carbon tetrachloride	1	18.9	3.1	0.02	93
Carbon tetrachloride	3	35.5	16.1	0.15	87
Carbon tetrachloride	5	41.4	32.8	0.35	80
Cyclohexane	1	5.6	8.1	0.01	92
Cyclohexane	3	20.5	40.0	0.22	83
Cyclohexane	5	32.7	41.4	0.35	75
THF	1	19.6	8.1	0.04	84
THF	3	41.5	38.6	0.42	78
THF	5	60.8	61.5	0.98	67
DMF	1	24.3	1.2	0.01	91
DMF	3	29.9	25.6	0.20	73
DMF	5	36.4	42.8	0.41	60
Benzene	1	7.3	10.6	0.02	85
Benzene	3	9.8	47.8	0.12	74
Benzene	5	11.6	51.8	0.16	62

[a] Contact angle of PE film before grafting at 94°. [b] Contact angle of inner side of PE film; polymerization conditions: content of BP, 3 wt% of VAc; volume of VAc, 25 μL; polymerization temperature, 30°C ; intensity of UV radiation, 5110 μW cm^{-2}.

vent and LDPE film is too high, the effective amount of BP becomes limited (hexane and chloroform); if the affinity is too low, the active hydrogens abstracted by [BP]^T are limited (DMF). Therefore, only those reagents with moderate affinity to LDPE film are effective.

Different Solvents of VAc

Various reagents were applied as solvents of VAc, including acetone, cyclohexanone, cyclohexane, methanol, ethyl acetate, carbon tetrachloride, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), and benzene. The results are listed in Table III.

From CP, GE, and GP in Table III, it seems that the behavior of these different solvents is related to solubility parameter (SP), absorbing of UV radiation and reactivity and initiating ability of the solvent.

Solubility Parameter (SP)

According to the solubility parameters (SP, Table II), these reagents can be classified as, carbon tetrachloride and cyclohexane have higher affinity to LDPE film; acetone, methanol, ethyl acetate, THF and benzene have medium affinity; and DMF has lower affinity. The different affinities lead to different influence on graft polymerization.

The swelling of film samples caused by solvents is probably another factor of graft polymerization. H. Kubota[6] investigated the influence of swelling on grafting vinyl monomers onto cellulose. In this study, several reagents whose SPs are similar to that of PE film help to swell the film, which is favorable for VAc to penetrate into the deeper layers of the film. In our earlier study,[3] pre-irradiation was used to complete grafting VAc onto

Table IV. Molar extinction coefficients of reagents

Reagent	Solvent	Maximum wavelength/nm	Molar extinction coefficient (log ε)
Benzene	Oil ether	255	2.35
Acetone	Ethanol	271	1.20
Acetone	Cyclohexane	270	1.99
Cyclohexanone	Hexane	285	1.15
Ethyl acetate	Cyclohexane	220	1.69
Benzophenone	Chloroform	254	4.18

LDPE film, using DMF and ethyl acetate as solvents, respectively. Under the same conditions, graft polymerization proceeds more smoothly in ethyl acetate than in DMF. The SP of ethyl acetate (SP=9.1) is much closer to that of LDPE (SP=7.9) than that of DMF (SP=12.0). Accordingly, it is easier for ethyl acetate to diffuse through LDPE film than DMF. During diffusion, ethyl acetate makes LDPE film swell to a certain degree, which is favorable to graft polymerization.

Absorbing of UV Radiation

As solvents of VAc, acetone, cyclohexanone, ethyl acetate, DMF and benzene absorb UV radiation (200—400 nm) at certain wavelengths. The molar extinction coefficients (ε) and maximum absorption wavelengths of these reagents are presented in Table IV.

Although the extinction coefficients are negligible compared with that of BP ($\varepsilon = 17000$ L mol^{-1} cm^{-1}, $\lambda = 254$ nm), their amounts are much more than that of BP. Therefore, absorbing UV radiation by these solvents is probably important for graft polymerization. Table III shows that benzene is not a suitable solvent of VAc. When benzene is applied as solvent of VAc, polymerization proceeds with much difficulty. When the reaction system is irradiated for 5 min, only 11.6% of VAc takes part in polymerization, of which about 51.8% is grafted polymer. It seems closely related to the absorption of UV radiation by benzene at around 255 nm. Based on our previous research,[2] when far UV radiation (200—300 nm) is excluded with a piece of polyethylene terephthalate (PET) film, the graft polymerization of VAc on LDPE film is restrained greatly. Consequently, the strong absorption of UV radiation at 255 nm by benzene (log $\varepsilon = 2.35$, Table IV) may lower the initiating efficiency of BP. Graft polymerization proceeds just on the surface of the film because the screen of UV radiation by benzene makes the reaction difficult in the deep layers. As a result, the grafted chains diffuse mainly on surface regions, and are confirmed indirectly by the contact angles in Table III.

Reactivity and Initiating Ability

Considering the initiation mechanism of BP,[1] it should

be noted that in polymerization systems, solvents containing active hydrogens should be avoided. In Tazuke and colleagues' article,[8] it is thought that methanol, as solvent, inhibits graft polymerization; but in Davis' studies,[4] methanol was used as solvent to graft styrene on cellulose. It is obvious from the data in Table III that methanol affects graft polymerization slightly. The reason may be that the bond energy of H–CH$_2$OH is so high that it is not easy for [BP]$^{\mathrm{T}}$ to abstract hydrogens from CH$_3$OH.[9]

According to Table III, DMF is not suitable as solvent of VAc, which is related closely to the fact that it cannot penetrate through PE films. Pashova[10] considers that DMF is an undesirable component of the solvent for polymerization, because nitrogen atoms on DMF may participate in the interactions with primary radicals formed when BP is irradiated by UV radiation.

It is thus concluded that acetone is the most useful solvent in graft polymerization, in agreement with the results by Tazuke and colleagues.[11] In their opinion, acetone has high stability against hydrogen abstraction by excited sensitizers. The ability of acetone to initiate graft polymerization when irradiated by UV radiation may make contribution to it as mentioned by Allmer.[12]

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