Functionalization of Polymer Supports for Polymerization Catalysts by Graft Polymerization Method

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Synopsis

The specific features of the gas-phase radiation-induced and plasma-initiated graft polymerization of certain monomers possessing the functionality needed for immobilization of transition metal compounds were studied. The radiation yields of allyl monomers grafted to polyethylene, polypropylene, and poly(vinyl chloride) (5–25 molecules/100 eV) were found to be close to the radiation yields of the polymerization of these monomers in a liquid state. The kinetics of methyl methacrylate and acrylic acid postgrafting to polyethylene pretreated with helium discharge plasma were also studied. The graft-initiating effect of PE powder treated with plasma for 5–10 min was found to be comparable with that of γ-irradiation in a dose 0.5–4 Mrad. The results of immobilization of transition metal compounds [$TiCl_4$, VCl_4, $VO(OC_2H_5)_3$, $Ti(OC_4H_9)_4$, etc.] on carriers prepared by the method of polymer support functionalization by grafting are described. The extent of completion of the immobilization reaction is found to vary from 0.1 to 0.96 and to depend both on the nature of the transition metal and on the specificity of the grafted fragments.

INTRODUCTION

A new trend in the catalysis by transition metal complexes, their immobilization on the surface of different carriers, has been developed during the last several years.[1-5] Of particular scientific interest is the elucidation of details of these processes which may be regarded as the formation of a new ligand sphere. From a practical point of view, the study in this direction is especially fruitful and leads to new catalytic systems which can improve chemical engineering and polymer chemistry. Polymer carriers with active sites may be prepared in some different ways. The first is polymerization and/or copolymerization of monomers with the needed functional groups. However, a number of problems arise in this way, such as synthesis of initial monomers, the interaction of catalytically active sites with the monomer double bonds in the course of polymerization, solubility requirements, etc.

The second way is the attachment of a functional group onto the surface of porous granular polymer globes crosslinked by the optimal amount of crosslinking agent to meet the requirement of mechanical rigidity and permeability. The difficulties which are encountered are side reactions leading to inhomogeneity of polymer carriers and incompleted reactions.

When the polymer carrier is devised, it seems to be rather desirable to attach definite functional groups onto the developed surface of polymer support. The radiation-induced gas-phase graft polymerization technique seems to be most convenient for this purpose.[6-9] This technique comprises the irradiation of

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polymer support in contact with the gas monomer by x-rays, γ-rays, or fast electrons. The active species, i.e., free-radical ions, are formed on the surface upon irradiation, and graft polymerization is thereby initiated. An important feature of the method is the fact that it yields virtually no homopolymer, and the polymer layer formed is therefore chemically bound to the polymer support. The advantages of the method are that almost every polymer may be used as support and that a wide variety of monomers can be grafted onto the surface. Since only the surface of the polymer support should be activated, the process can be initiated by glow discharge plasma.

The present work examines gas-phase graft polymerization as a method for producing polymer carriers for chemically attached active catalytic sites.

EXPERIMENTAL

Carrier Preparation. Monomers were purified and dried by standard methods. Powdered low-density polyethylene (PELD) with specific surface of 1.9 m^2/g, high-density polyethylene (PE) of 4 m^2/g, copolymer of ethylene with propylene (CEP) of 1.3 m^2/g containing 5 mole % propylene, polypropylene (PP) of 1.3 m^2/g, poly(vinylchloride) (PVC) of 6 m^2/g, and polystyrene (PS) of 130 m^2/g were used as supports in graft polymerization experiments. The specific surfaces were evaluated from the data on low-temperature nitrogen adsorption. Grafting was initiated by γ-irradiation of ^{60}Co (dose rates of 2.4–33 krad/min), by fast 3.5 MeV electrons (dose rates 0.1–10 Mrad/min), and by glow discharge plasma. All other details have been reported elsewhere.[5]

Immobilization of Transition Metals Complexes on Polymer Support. The reactions between polymer support and transition metal compounds were carried out in dried heptane or carbon tetrachloride in the absence of atmospheric oxygen. The polymer with a grafted functional layer was initially vacuum sealed during 3–4 hr at 60–80°C and 0.1 torr of residual pressure. Metal compound solutions, 0.5–2.0%, were mixed with 3–5% suspension of polymer powder in the solvent and allowed to react during 2–3 hr upon intense stirring. The product was filtered with a vacuum glass filter in an inert atmosphere, washed, and dried *in vacuo* to constant weight. The metal content was checked by atomic absorption spectrophotometry.

IR Spectral Analysis. Powders of polymer supports and grafted polymers were pressed into films 50–70 μm thick or suspended in purified and dried vaseline. The apparatus used was a UR-20 or a Perkin–Elmer 325 spectrophotometer.

RESULTS AND DISCUSSION

Radiation-Induced Vapor-Phase Graft Polymerization Initiated by Irradiation from γ Rays and Fast Electrons

Allyl Monomer Grafting

Macromolecular carriers with hydroxy, amino, and sulfhydryl coverages were obtained by radiation-induced vapor-phase grafting of allyl alcohol (AAl), allyl- and diallylamine (AA, DAA), and allyl sulfide (AS) onto powdered polymer supports. A particular feature of these monomers is that they are known[10-12]
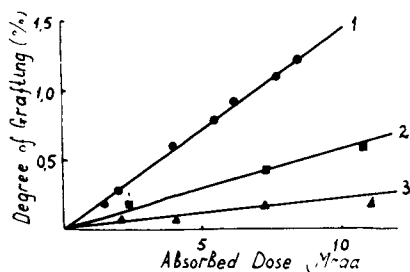
Fig. 1. Amount of grafted polymer PAAl (1), PAA (2), and PDAA (3) onto PE powder vs. dose: temp. 20°C, dose rate 3 krad/min.

to have low radiation yields of bulk polymerization (G_p = 5–25) which are independent of dose rate. This implies that the length of polymer chains obtained does not exceed 10–12 monomeric links.

The experimental data on allyl monomer grafting are presented in Figures 1 and 2, where it can be seen that the grafting radiation yields (G_{gr}) are essentially constant up to 1–2 wt % grafted polymer and have a value of 5–25 molecules/100 eV energy absorbed in the sample comprising polymer support and 0.05–0.10 wt % sorbed monomer. The obtained G_{gr} values are in good agreement with reported G_p values.[10–12] It also follows from Figures 1 and 2 that the G_{gr} values for PAAl change only slightly with changes in the polymer support and have a value of 15–25 excluding the system PELD + AAl (Figs. 2 and 3) where the G_{gr} value is remarkably lower, being only 10 molecules/100 eV. A good agreement between G_p and G_{gr} values is not unexpected since it arises from the distinctive feature of grafting radiation polymerization[9]: Owing to diffusion of active species from the support to the surface and/or monomeric molecules into the polymer support, the active species from the lower-lying layers of the support take part in the initiation of graft polymerization.

We have recently found[5] that the G_{gr} for polyallyl alcohol onto PE is independent of the dose rate within the range of 0.2–6.5 Mrad/min. This is very important since it permits increasing the grafting rates by using more energetic irradiation sources. For example, a carrier containing 2 wt % of PAAl (PE–gr–PAAl) has been prepared in a few minutes upon irradiation by 3.5 MeV fast electrons (Table I).

The behavior of other allyl monomers in graft polymerization can be seen from Table I.
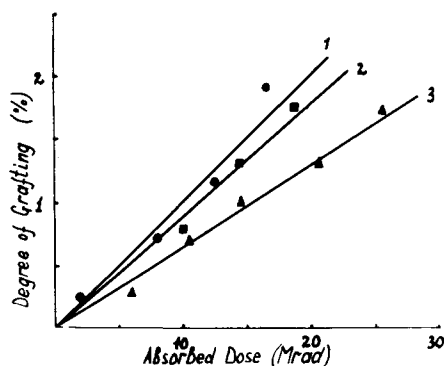

Fig. 2. Amount of grafted polymer PAAl onto PVC (1), PP (2), and PELD (3) powder vs. dose: temp. 20°C, dose rate 1 Mrad/hr.
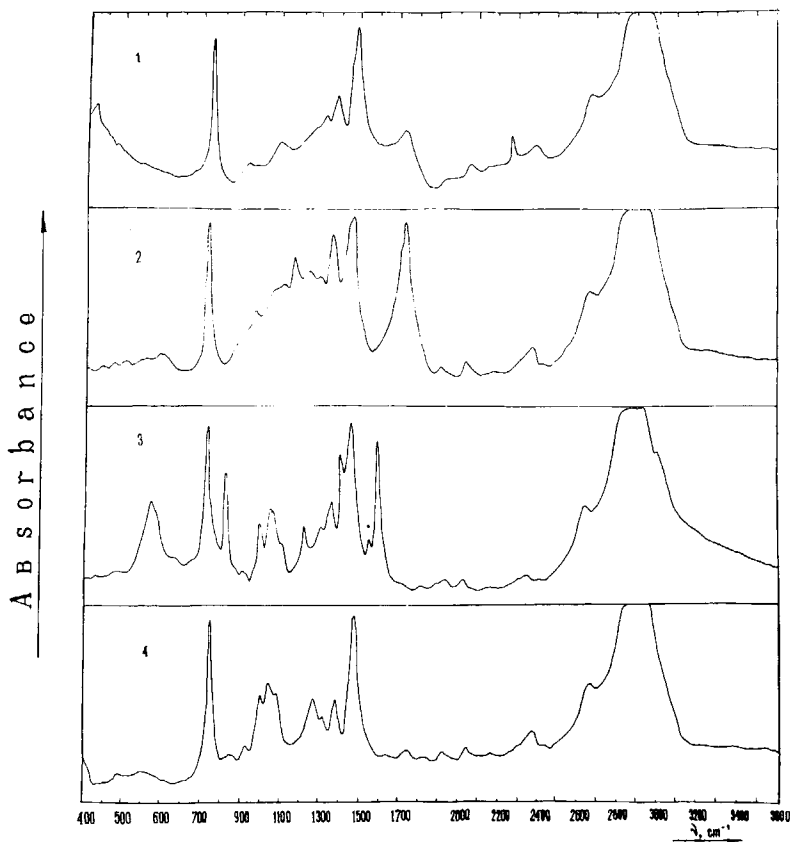
Fig. 3. IR absorption spectra: PE–*gr*–PAN (1), PE–*gr*–PMVK (2), PE–*gr*–P4-VP (3), and PE–*gr*–PDEVPAc (4); thin film.

Grafting of Other Monomers

The experimental data obtained are presented in Table I. As is seen, the grafting degrees and the G_{gr} values vary within wide ranges, from 0.1 to 13 wt % and from 2 to 1300 molecules/100 eV, respectively.

IR Spectra of Grafted Samples

IR absorption spectra for PE supports with a grafted layer of polyacrylonitrile (PAN)-1, PMVK-2, P4-VP-3, and PDEVPAc-4 are shown in Figure 3. In addition to 720 and 1480 cm^{-1} bands inherent to PE support, new absorption bands due to grafted components could be found: 2242 cm^{-1} stretching vibrations of nonconjugated C≡N bond in PE–*gr*–PAN; 1710 cm^{-1} stretching vibrations of C=O in PE–*gr*–PMVK. Grafting 4-VP onto PE is accompanied by the appearance of a number of absorption bands of the pyridine ring, 1580 cm^{-1} of the C=N and C=C bonds being the most prominent. The stretching vibrations of the P—O—C bond at 972 cm^{-1} and the P=O bond at 1253 cm^{-1} were found in the IR spectrum of PE–*gr*–PDEVPAc. Bands in the range of 1600–1700 cm^{-1} may be assigned to stretching vibrations of C=C and C=N double bonds. The appearance of these bonds may be tentatively explained by the grafting of AN onto PE via a C≡N bond which results in the formation of the fragment.

TABLE I
Parameters of Radiation-Induced Vapor-Phase Grafted Polymerization

Polymer support	Grafted monomer	T, °C Support	T, °C Monomer	I, rad/sec	D, Mrad	Amount of grafted monomer, %	G_{gr}
PE	AS	40	20	80	2.4	0.4	23
PE	diallyl sulfide (DAS)			220	10.0	1.2	11
PE	methyl vinylketone (MVK)			63	1.0	3.6	510
PE	vinyl acetate (VA)			220	6.0	12.5	200
CEP	VA				6.0	5.0	100
PP	VA				5.0	5.0	115
PS	VA				4.0	1.3	35
PE	methyl methacrylate (MMA)	50	20	60	1.0	13.0	1300
PE	2-vinylpyridine (2-VP)	50	30		5.0	2.0	20
PE	4-vinylpyridine (4-VP)	70	50	80	5.0	2.0	30
PE	propargyl alcohol	40	20	70	60	1.8	8
PE	dibutyl ether of vinylphosphoric[a] acid (DEVPAc)	40	40	80	10	5.0	
PE	AAl	20	20	10.5	12	2.0	25

[a] Liquid phase grafting on PE suspension in 5% dibutyl ether of vinylphosphonic acid in benzene.

$$-C\!\!=\!\!N-$$
$$|$$
$$CH$$
$$|$$
$$CH_2$$
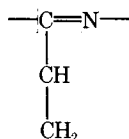
The absorption band of this fragment is within the frequency range mentioned.[13] This point of view is also supported by the yellowish color of PE–*gr*–PAN obtained.

Hence, it may be concluded that macromolecular carriers with a protolytic coverages (OH, NH$_2$, NH, SH, etc.) as well as polymer carriers containing fragments and atoms with unshared electron pairs (C=O, >N, >S, $-\overset{|}{C}\!\!=\!\!N-$, etc.) may be readily prepared by the method of vapor-phase graft polymerization induced by γ-rays and fast electrons.

Graft Postpolymerization Induced by Glow Discharge

The strongest damage of the PE surface in contact with glow discharge plasma was shown[14] to be caused by many factors such as UV radiation, electrons, ions, and excited gas molecules (mostly by UV). The same radiolysis products (i.e., radicals, crosslinks, molecules) as in the γ-irradiated samples had been detected in polymers exposed to plasma.[15,16]

Gas discharge plasma was used for initiation of the gas-phase graft postpolymerization, ensuring the needed functionality. The yields of grafted poly(acrylic acid) (PAAc) and poly(methyl methacrylate) (PMMA) versus the exposures of PE activated by plasma AAc and MMA vapors are presented in Fig-
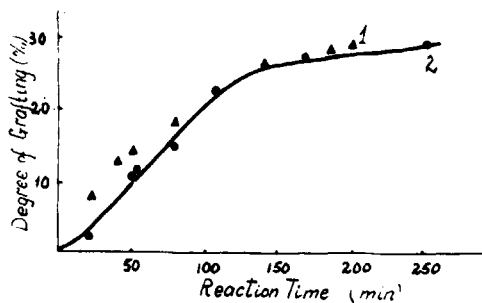
Fig. 4. Comparison of glow discharge and γ-initiated postgrafting kinetics of PAAc: PE exposure to plasma 10 min, He pressure 7 torr, 1; preliminary irradiation dose 4 Mrad, 2. Postpolymerization at 50°C.

ures 4 and 5. During the first 1–2 hr the amount of grafted polymer reaches 6–10 wt %, then the rate of the process remarkably decreases to 1–2 wt % per hr. The exposure time in plasma, the plasma energy, the helium pressure, the support temperature, and the monomer vapor pressure have their own effects on the grafting yield in postpolymerization initiated by plasma. In Figures 4 and 5 the data on plasma-initiated postpolymerization are compared with those obtained by γ-ray initiation. The comparison shows that graft postpolymerization of AAc and MMA onto PE is almost equally initiated both by the exposure to plasma during 10 min and by γ-irradiation up to a dose of 0.4–0.5 Mrad. In view of the complicated nature of plasma action on PE surface, a more detailed comparison of the postpolymerization mechanisms seems to be impossible. IR spectra of postgrafted samples obtained by γ- or glow discharge initiation are practically equal.

Immobilization of Complex Catalysts on Polymer Support

The reactions of substrate with grafted coverage via main (covalent bonding) or side (donor–acceptor bonding) valences offer the best ways for immobilization of complex catalyst on polymer carriers. The first way is realized in the reactions of highly valent transition metals with grafted layer containing hydroxy, amino,
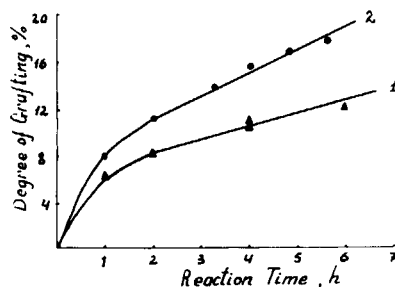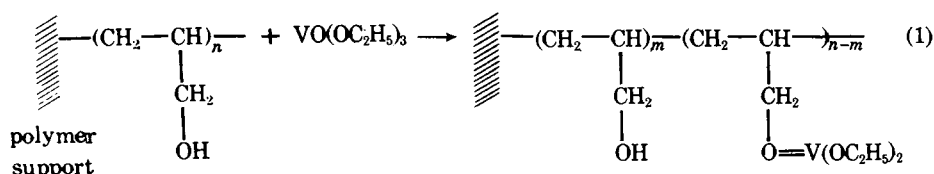

Fig. 5. Comparison of glow discharge and γ-initiated postgrafting kinetics of PMMA: PE exposure to plasma 5 min, He pressure 5 torr, 1; preliminary irradiation dose 0.4 Mrad, 2. Postpolymerization at 20°C.

amido, or carboxy groups, as is the case in PE–gr–PAAl and $VO(OC_2H_5)_3$:

$$\text{—(CH}_2\text{—CH)}_{\overline{n}}\text{ + VO(OC}_2\text{H}_5)_3 \longrightarrow \text{—(CH}_2\text{—CH)}_{\overline{m}}\text{—(CH}_2\text{—CH}\text{—)}_{\overline{n-m}} \quad (1)$$

polymer support

with branches CH_2—OH on left, and CH_2—OH / CH_2—$O{=}V(OC_2H_5)_2$ on right.

IR spectra of PE–gr–PAAl (a), together with products of its reaction with $TiCl_4$ (b) and $VO(OC_2H_5)_3$ (c), are given in Figure 6. Reaction (1) is accompanied by virtually complete disappearance of the diffuse absorption band at 3400 cm^{-1} and by appearance of additional bands at 472 cm^{-1} and 1035 cm^{-1} which may be assigned to Ti—Cl and V=O vibrations in fixed components.

Comparatively strong Lewis acids, $TiCl_4$, VCl_4, $MoCl_5$, $CoCl_2$, etc., may be immobilized on polymer supports containing electron donor groups >C=O, —OCOR, —COOR, C≡N, >N, etc. These carriers may be regarded as specific macroligands:
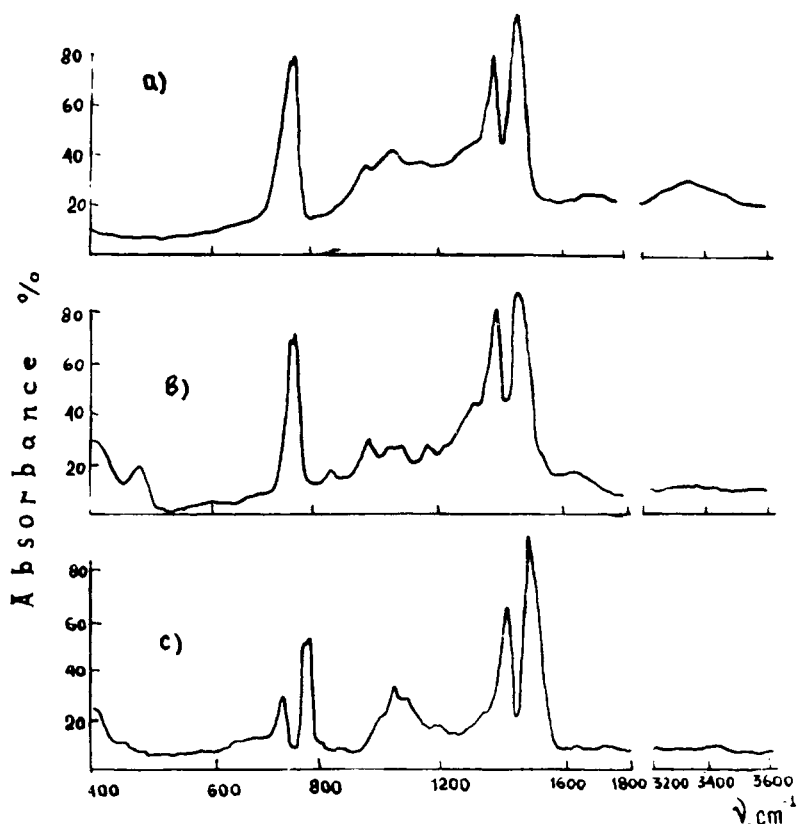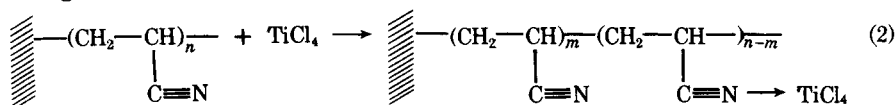
$$\text{—(CH}_2\text{—CH)}_{\overline{n}}\text{ + TiCl}_4 \longrightarrow \text{—(CH}_2\text{—CH)}_{\overline{m}}\text{—(CH}_2\text{—CH}\text{—)}_{\overline{n-m}} \quad (2)$$

with branch C≡N on left, and C≡N / C≡N → $TiCl_4$ on right.

Fig. 6. IR spectra of PE–gr–PAAl (a) and the products of its reactions with $TiCl_4$ (b) and $VO(OC_2H_5)_3$ (c). (a) thin film; (b,c) suspension in vaseline.
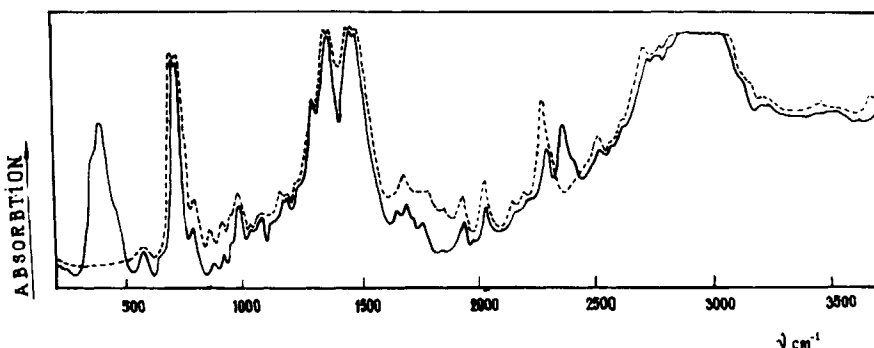
Fig. 7. IR spectra of PE–gr–PAN (dotted curve) and complex compound of $TiCl_4$ with PE–gr–PAN (solid line).

The occurrence of bonding of this type is supported by the shift of the nitrile vibration band from 2242 cm⁻¹ in PE–gr–PAN to 2287 cm⁻¹ in the complex (Fig. 7).

The results thus obtained are illustrated by Table II showing that the ratio (amount of bound metal)/(amount of functional groups) is dependent either on the kind of transition metal compound or on the specificity of the grafted components. It should be noted that under experimental conditions (60–80°C, heptane and CCl_4 as solvents), the grafted functional groups of allyl polymers are utilized more efficiently than those of vinyl monomers. The amount of bound metal decreases with immobilization of transition metal compounds containing large substituents [$Ti(OC_4H_9)_4$, $(C_5H_5)_2TiCl_2$, etc.], other things being equal.

Transition metal catalysts immobilized on grafted polymer carriers proved

TABLE II
Immobilization of Complex Catalyst Components on Polymers with Grafted Layer

Polymer carrier	Amount of grafted component, wt %	Immobilized compound	Bound metal content	
			(mole /g) × 10⁴	Functional groups, mole/mole
	2.5	$TiCl_4$	2.5	0.96
PE–gr–PDAA	3.1	VCl_4	3.8	1.19
	3.1	$Ti(C_5H_5)_2Cl_2$	0.10	0.031
	4.0	VCl_4	2.5	0.36
PE–gr–PAA	4.0	$Ti(OC_4H_9)_4$	0.1	0.014
	4.0	$Ti(C_5H_5)_2Cl_2$	0.1	0.014
	3.6	$TiCl_4$	0.6	0.10
PE–gr–PAAl	3.6	VCl_4	3.0	0.50
	3.6	$Ti(OC_4H_9)_4$	0.15	0.025
PS–gr–PAAl	1.8	$VOCl_3$	1.6	0.52
PP–gr–PAAl	1.6	$TiCl_4$	0.8	0.29
	6.6	$VO(OC_2H_5)_3$	0.7	0.08
PE–gr–PAAc	9.1	$\overset{\lor}{V}O(OC_2H_5)_3$	1.2	0.10
PE–gr–PAAc	0.4	$TiCl_4$	0.15	0.30
PE–gr–PAN	10.0	$TiCl_4$	3.6	0.19
	3.4	VCl_4	0.2	0.03
PE–gr–PVA	11.0	$TiCl_4$	1.7	0.13
PE–gr–PDAS	1.2	VCl_4	0.52	0.25
PE–gr–P4-VP	2.0	$TiCl_4$	0.50	0.26

to have high and stable catalytic activity in polymerization catalysis. Details will be reported in the future.

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