

Synthesis and properties of novel end-functionalized polybutylacrylate and its metal complexes

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Summary

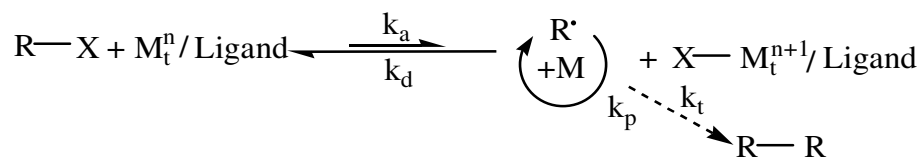
Well-defined polybutylacrylate (PBA) was prepared by atom transfer radical polymerization (ATRP). A novel end-functionalized PBA (macromolecular ligand) was synthesized via PBA bonded with thiocarbamide. Since thiocarbamide possesses strong chelating ability, end-functionalized PBA possesses some new properties such as coordination with metallic ions. After metallic ions were introduced into it, two kinds of end-functionalized PBA metal complexes were got. The structure and property of PBA, end-functionalized PBA and its metal complexes were characterized by ¹H NMR, UV, GPC, Atomic Emission Spectrometry (AES), Cyclic Voltammogram (CV) and Dielectric Constant. The results indicate that the properties of end-functionalized PBA with well-defined structure were improved greatly by introducing a small quantity of transitional metallic ions into it. The novel end-functionalized PBA metal complexes exhibit stable electrochemical activity, dielectric property and have a good prospect in many fields as functional polymer.

Introduction

Polymer Metal Complexes (PMCs) have been the subject of increased interest in the fields of catalytic reactions, electrochemical materials, optimized sensory materials, chemical sensors, magnetic materials and in connection with biochemistry and environmental chemistry due to their excellent particular properties[1-4]. The structure character and application of PMCs have become an important focus of study presently. Most of PMCs, consisting of the polymer backbone with chelate ligands, which might coordinate to metallic ions, have been synthesized and characterized [5-6]. In general polymer main chains or side chains contain functional groups that can complex with metallic ions directly. The using fields of PMCs include conductive adhesive and materials of electrode. The preparation of polymer-modified electrodes that function as electro catalysis, chemical sensors and electrochemical displays remains an active field of research[7-9]. Usually ligands of polymer metal complex are composite of N, P, O and S with lone-pair electron such as pyridine, PPh₃, -NH₂, -OH, -SH and carboxylic acid etc[10]. And the transitional metallic ions such as Co²⁺, Cu²⁺, and Ag⁺ etc[11] can be introduced into the polymers. It is believed that redox potential

of an organic polymer is the same or below as of metal center. Metallic ions were introduced into polymer that should create materials with enhanced electron mobility. Thereby, optimized sensory and catalytic materials were synthesized one by one. The design of new functional polymer architectures containing transitional metals in well-defined coordination environments has attracted much attention[7]. Although there is an obvious tendency that polyacrylate and polymethacrylate are used as general material, its metal complex has few reports. Because those polymers prepared by conventional radical polymerization have not functional groups to coordinate with metallic ions. But living polymerization provides a chance to synthesize polyacrylate or polymethacrylate metal complex.

Polymer metal complex is focusing more and more toward the development of architectural systems, possessing properties that arise from their well-defined structures[12]. Living and controlled polymerization techniques are appropriate tools in order to obtain polymers and copolymers with precise architectural characteristics, engineered with the properties required for a given application. Among them, atom transfer radical polymerization (ATRP) has proven to be a powerful tool for the construction of a great number of macromolecular systems having a variety in composition, topospecificity, end-functionalities and architectures, but at the same time using easily accessible experimental conditions. For example economopoulos et al. synthesized successfully end-functionalized Polyquinolines using ATRP[13]. At present the study of atom transfer radical polymerization is focusing on functional polymer chemistry and physics for its potential applications in the tailormade design of polymeric structures, functional materials and so on[14]. As reference[15] report that mechanism of ATRP as follows:



Scheme 1 The mechanism of ATRP (R-X: initiator X: Cl, Br; M: monomer; $\text{M}_t^n / \text{M}_t^{n+1}$: catalyst)

From scheme 1, ATRP can synthesize polymers with low polydispersities, predetermined molecular weights. Furthermore ATRP tolerated various functionalities in its monomeric parts without disturbing the polymerization reaction. The terminal group of polymer that was prepared by ATRP is halogen atom and another end is also prescient, which both come from initiator. In another word, polymers that were synthesized by ATRP own well-defined structures. Therefore, ATRP may be an effective way to synthesize architecturally functional polymers or oligomers. Some functional radical initiators such as azo compounds or functional transfer agents to synthesize end-functionalized polymers have been reported[16]. As well known, the polyacrylate and polymethacrylate are general materials that were used in many fields as coating, adhesive and damping materials for its flexibility, transparency and adhesion[17]. But in conventional radical polymerization, it does not result in polymers with well-defined structures. Using ATRP, it is possible to synthesize those polymers with end-functionalized, desired molecular weights and low polydispersities. After transitional metallic ions were introduced into end-functionalized polymers, end-functionalized polymer metal complexes were synthesized.

In this paper, polybutylacrylate with well-defined structures was synthesized by ATRP. Via the halogen on the end of PBA combining with thiocarbamide, end-functionalized PBA was synthesized. It was used as novel macromolecular ligand for its chelate activity. End-functionalized PBA metal complexes were prepared after two kinds of transitional metallic ions were introduced respectively. Evidence from ^1H NMR and GPC has proved that PBA was synthesized by ATRP successfully. The results of UV, CV and Dielectric Constant show that properties of PBA were improved greatly by metallic ions. Moreover, the excellent electrochemical activity of the novel end-functionalized PBA metal complex is of great interest.

Experiment

Materials

n-Butyl acrylate supplied by Shenyang Chemical Co. (A.R., 99.0%) was washed by 5% aq solution of sodium hydroxide, stirred over calcium hydroxide for 24 h, distilled under vacuum and stored at $-15\text{ }^\circ\text{C}$ before use. CuCl purchased from Shanghai Chemical Co. (A.R., 97.0%) was purified by stirring in acetic acid, filtered, washed with ethanol and dried. 2,2'-Bipyridine (bpy) (A.R., 97.0%) and thiocarbamide (A.R., 98.6%) provided by Beijing Chemical Co. CuCl_2 (A.R., 99.0%) and CoCl_2 (A.R., 99.0%) supplied by Tianjin Chemical Co. DL-ethyl-bromopropionate (99.0%) was provided by ACROS. all reagents were used directly without purified. N,N-dimethylformamide (DMF) was freshly distilled before use.

Equipment

^1H NMR was performed on a Bruker AV400 instrument using CDCl_3 as the solvent. Molecular weights and molecular weight distributions were measured on Waters 410 GPC (Guard, 10^5 , 10^3 , 10^2 Å) using THF as the eluent and polystyrene as standard. The ultraviolet spectrum (UV) was recorded on a Shimadzu UV-Vis UV-3100 spectrometer. The content of metallic ions was investigated by atomic emission spectrometry (AES) model PE-1000 coupling inductance (America). The cyclic voltammogram (CV) was obtained on a HPD-1A Model bipotentiostat with a TYPE3086-23A₄ X-Y recorder. The glassy carbon electrode served as the working electrode, Pt wire served as the counter electrode and the reference electrode used as Ag/Ag^+ (0.01M AgNO_3 in ethanol). Dielectric Constant: Instruction Manual for BI-870 Dielectric Constant Meter. Brookhaven Instruments Corporation (American).

Synthesis of polybutylacrylate from ATRP

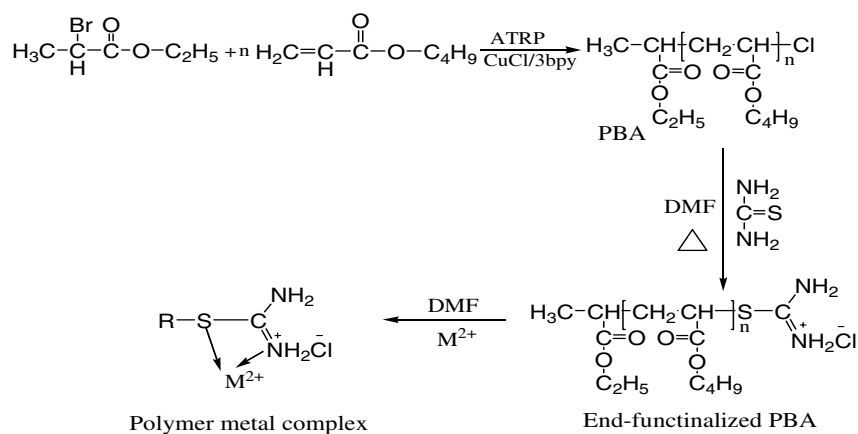
A bottom flask was charged with 33.8 mg of CuCl and 160.0 mg of bpy. The flask was sealed and cycled between vacuum and argon thrice to remove the oxygen. Then 4.9 ml of degassed n-butyl acrylate and 42.7 μl of dl-ethyl-bromopropionate (initiator) were added by using syringes. The flask was immersed into a $80\text{ }^\circ\text{C}$ oil bath with sufficient stirring. After 6 h, the polymerization was cooled in a hydrohalite bath to terminate the polymerization. The mixture was diluted with THF and precipitated with solution of methanol and deionized water. After dissolved and precipitated for thrice, the target polymers were dried under vacuum at $60\text{ }^\circ\text{C}$ for 24 h.

Synthesis of end-functionalized polybutylacrylate

A dry round bottom flask was charged with 2g of thiocarbamide, 1g of polymer and 20ml of N,N'-dimethylformamide. The reaction last for 6 h at 90 °C with sufficient stirring. Then the reaction was cooled to room temperature and concentrated under vacuum. The concentrated product was diluted in THF, and precipitated in methanol. The target product of end-functionalized PBA was dried under vacuum at 60 °C for 24 h.

Synthesis of end-functionalized polybutylacrylate metal complexes

0.5g of end-functionalized polybutylacrylate, 2g of CuCl₂ or CoCl₂ and 20ml of N,N'-dimethyl formamide were added in a bottom flask and last for 4 h at room temperature. The solution was filtered to remove surplus chloride. Correspondingly, the solution was concentrated under vacuum, diluted in THF and precipitated in methanol. The brown end-functionalized PBA metal (Cu²⁺) complex and the grassy end-functionalized PBA (Co²⁺) polymer metal complex were obtained and dried under vacuum at 60 °C for 12 h. All the synthetical routes show in Scheme 2.



Scheme 2 The route of synthesis of end-functionalized PBA and its metal complex

Results and Discussion

Characterization of polybutylacrylate from ATRP

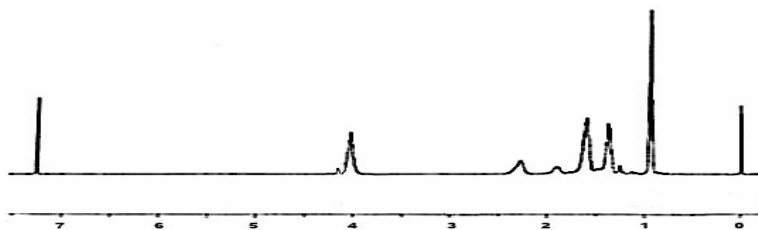


Fig. 1 The ¹H NMR of PBA from ATRP

As references reported[18-19], dl-ethyl-bromopropionate (initiator), CuCl (catalyst) and 2,2'-bipyridine (ligand) were employed in ATRP of n-butyl acrylate, which had been proved its living/controlled polymerization at 80 °C.

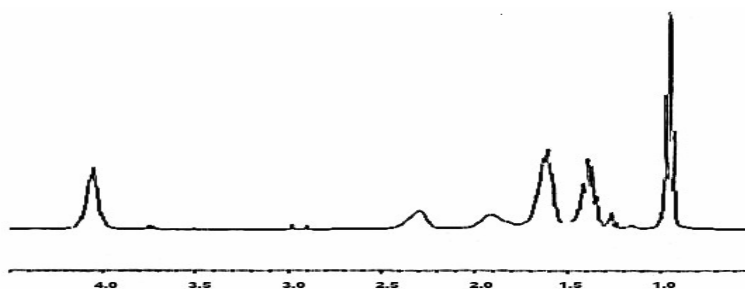


Fig. 2 The ^1H NMR of end-functionalized PBA

The structures of PBA with low polydispersities were analyzed by ^1H NMR spectroscopy using CDCl_3 as solvent (Fig. 1). It was carefully examined to determine whether the PBA was ended by fractional initiator. The broad multiplet peaks, centered at 4.0 ppm ($-\text{CH}_2\text{O}$), 2.28 ppm ($-\text{CH}$), 0.9-1.89 ppm ($-\text{CH}_2$) and 0.86 ppm ($-\text{CH}_3$) corresponded to PBA chain protons, at same time, the triplet peak at 4.16 ppm corresponded to the terminal group of $-\text{CH}(\text{COO})\text{Cl}$. The characteristic peak of initiator segment ($\text{CH}_3\text{CH}-$) at the end of chain could be pointed out at 1.05 ppm. From the ^1H NMR, the groups of halogen and $\text{CH}_3\text{CH}-$ on the end of PBA are initiator segments of ATRP[19-20], which clarified dl-ethyl-bromopropionate initiated n-butyl acrylate for ATRP. From data of GPC the polydispersity and M_n of the PBA is 1.38 and 10960 respectively. Furthermore, the tested molecular weight (10960) is closed to design molecular weight (10240). The well-defined polymer with symmetrical molecular weight owns excellent properties comparing with polymer synthesized by traditional radical polymerization.

Characterization of end-functionalized polybutylacrylate and its PMCs

Thiocarbamide can bond with haloid alkyl and form compound with double amidocyanogen, which possess chelating activity to metallic ions (Scheme 2).

Fig. 2 is the ^1H NMR of end-functionalized PBA. Two peaks at 2.99 ppm and 2.9 ppm which were attributed to protons of amidocyanogen indicated the thiocarbamide was attached to PBA and novel macromolecular ligand was prepared[21].

Fig. 3 is the UV spectra of end-functionalized PBA and its metal complexes. In facet, PBA has only one absorption peak from 190 nm to 400 nm. But the spectrum of end-functionalized PBA appears three peaks at 210 nm, 220 nm and 231 nm respectively. The peak at 210 nm is the characteristic absorption of ester, which is the main chain of PBA; The peak at 220 nm was assigned to $n-\sigma^*$ of $\text{C}-\text{NH}$; And the peak at 231nm was attributed to the $\text{HN}=\text{C}-\text{NH}_2$ [22]. Those data proved thiocarbamide was attached to PBA and end-functionalized PBA, i.e. novel macromolecular ligand, was synthesized. When metallic ions were added in the end-functionalized PBA, the amino group and sulphur element will coordinate with metallic ions. The bonds of the metallic ions

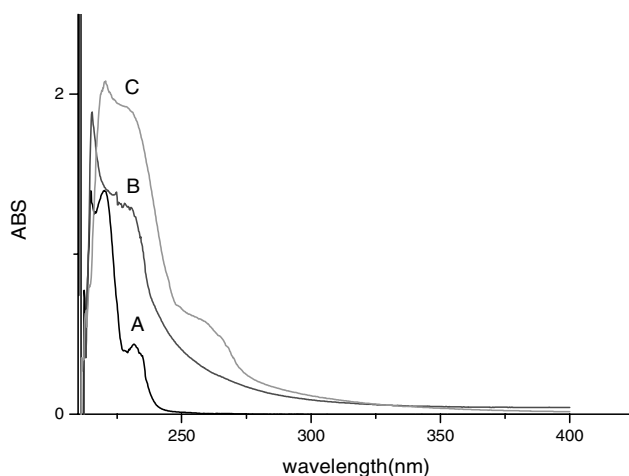


Fig. 3 The UV spectra of PBA and its metal complexes (A) end-functionalized PBA; (B) end-functionalized PBA Cu^{2+} complex; (C) end-functionalized PBA Co^{2+} complex

with end-functionalized PBA exhibit not only electrovalent bond character but also covalent bond character. From Fig. 3, it is clear that the absorptions of end-functionalized PBA are different from its metal complexes. As new complex bond was formed, the intensity of C-N and C=N were decreased. It exhibits more gentle ultraviolet absorb than the end-functionalized polymer. The UV change should only be attributed to the coordination of transitional metallic ions with amino group and sulphur element. the absorptions of end-functionalized PBA have shifted from 220 nm and 231 nm to 229 nm (Co^{2+}) and 227 nm (Cu^{2+}), which indicates that the group of $\text{HN}=\text{C}(\text{S})\text{NH}_2$ has participated in the bond with metallic ions. Because the central metallic ions can back-donate electrons to macromolecular ligands, the absorption peak of end-functionalized PBA is very broad compared with end-functionalized PBA. The ultraviolet absorptions of polymer Cu^{2+} complex and polymer Co^{2+} complex are different also, as the intensity of chemical bond of end-functionalized PBA metal (Co^{2+}) and end-functionalized PBA metal (Cu^{2+}) complex is different. A new broad absorption peak at 268 nm appears in UV spectrum of end-functionalized PBA metal (Co^{2+}) complex which is attributed to $d \rightarrow d$ transition of Co^{2+} . While the $d \rightarrow d$ absorption peak of the PBA metal (Cu^{2+}) complex has been overlapped by the absorption peak of macromolecular ligand (end-functionalized PBA) because the atomic number of cobalt is less than that of copper, the distinction between the energies of end-functionalized PBA and Cu^{2+} is smaller correspondingly.

As the content of end-functionalized group in macromolecular ligands is very low, metallic ions in end-functionalized PBA metal complex are also in a low concentration. The results of atomic emission spectrometry suggest that the content of Cu^{2+} in end-functionalized PBA metal (Cu^{2+}) complex is 2.440mg/g and the content of Co^{2+} in end-functionalized PBA metal (Co^{2+}) complex is 0.355mg/g. It's obviously that the structures and chelating ability between $\text{HN}=\text{C}(\text{S})\text{NH}_2$ and Cu^{2+} or Co^{2+} in end-functionalized PBA are different. As content of cooper is almost seven times of cobalt in end-functionalized PBA, it surely possesses close and well-defined structure. This viewpoint was proved also by CV.

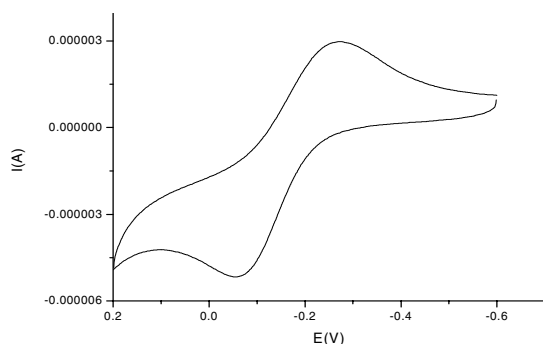


Fig. 4 The CV spectrum of end-functionalized PBA Cu^{2+} complex

Cyclic voltammogram (CV) is an important characterization of electrochemistry, which can afford information not only electrochemical activity but also the energy level of HOMO and LUMO of the polymer metal complexes[23].

Fig. 4 is CV of end-functionalized PBA Cu^{2+} complex. The reduction potential is at -0.061 V which is the LOMO value of end-functionalized PBA metal (Cu^{2+}) complex, and the oxidation potential is at -0.273 V which is the HOMO value of end-functionalized PBA metal (Cu^{2+}) complex. It shows that a redox progress between macromolecular ligands and Cu^{2+} has taken place. Most reports of polymers[24], the electrochemistry of the samples displays ligand-based with metallic ions redox processes. Because the redox potential of end-functionalized PBA Cu^{2+} complex is quasi-reversible, the transfer of electrons between the central metallic ions and macromolecular ligand is fast. The standard redox potential E^0 (Ox/Red) was calculated by $E_{1/2}(\text{Ox/Red})$, which can be obtained from equation (1).

$$E^0(\text{Ox/Red}) = E_{1/2}(\text{Ox/Red}) = (E_{pa} + E_{pi})/2 \quad (1)$$

That is $E^0(\text{Ox/Red}) = -0.167$ V. Furthermore, on continuously scanning in this range of potential, the I_p and E_p are almost the same. This indicates that the end-functionalized PBA Cu^{2+} complex is electrochemical activity[21]. Thus, this kind of polymer metal complexes can be used as electrode materials and in electric catalytic chemistry.

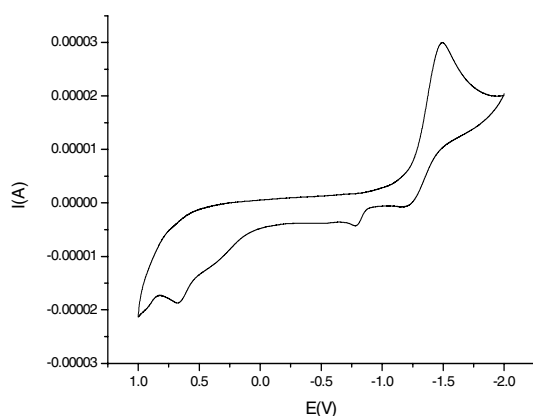


Fig. 5 The CV spectrum of end-functionalized PBA Co^{2+} complex

Fig. 5 is CV of end-functionalized PBA Co^{2+} complex. Compared with those of the end-functionalized Cu^{2+} complex, the reduction potential of the end-functionalized Co^{2+} complex is at -1.498 V, the oxidation potentials are at -1.238 V, -0.798 V and +0.665 V respectively[25], which shows that the Co^{2+} complex has undergone a gradual oxidation process. They are all negative reversible redox potential, which indicate that the transfer of the electrons between the metallic ions and the macromolecular ligand of the end-functionalized PBA Co^{2+} complex is difficult. Also these data show that the order of complex bond strength is $\text{Cu} > \text{Co}$ that is in agreement with the UV spectra. It's due to the central metallic ions can back-donate electrons to the macromolecular ligand.

Dielectric constant is a very important coefficient of dielectric polymer. Inductive electric charges appeared on the surface of the medium (dielectric materials) which was added in the parallel electrode board with electric field[26]. Usually, polybutyl-acrylate can be used as dielectric materials. Because the functional group of $\text{HN}=\text{C}(\text{S})\text{NH}_2$ possesses chelating ability, transitional metallic ions can be introduced into the end-functionalized PBA. A small quantity of metallic ions could change the polarity and density of inductive electric charges of the polymer metal complex[27]. In other words, dielectric properties of end-functionalized PBA will be improved greatly by metallic ions.

Table 1 shows the data of dielectric constants containing acetone, PBA, end-functionalized PBA and its metal complexes. The different values of dielectric constant reflect different polarity of those materials. End-functionalized PBA has the laegest value (22.7) and polymer metal complex is the smallest (20.6 of Co^{2+} complex or 20.8 of Cu^{2+} complex). As temperature increase, the dielectric constant decrease, which show that temperature is the greatest factor for the dielectric constant. Fig. 6 is the curves of dielectric constants at different temperature. All of the curves suggests the dielectric constants can be described by coefficient of temperature (TK ϵ). The experiential expression of coefficient was showed as follows[26]:

$$\text{TK}\epsilon = \Delta\epsilon / (\epsilon_0 \Delta t) = (\epsilon_t - \epsilon_0) / \{ \epsilon_0 (t - t_0) \} \quad (2)$$

Here ϵ represents dielectric constant and t is temperature (K). The coefficients of temperature were obtained from equation (2) seeing table 1.

Table 1. The dielectric constants and temperature coefficients of PBA, end-functionalized PBA and its complexes with different temperature

Sample	ϵ_1 297K	ϵ_2 302K	ϵ_3 307K	ϵ_4 312K	ϵ_5 317K	TK ϵ * 10^{-3}	Concentration (g/ml)*
Acetone	21.0	20.8	20.4	20.0	19.6	-3.3	---
PBA	22.2	21.6	21.0	20.5	20.0	-4.9	0.016
End-functio- nalized PBA	22.7	22.5	22.2	21.9	21.6	-2.6	0.008
Polymer metal complex (Cu^{2+})	20.8	20.4	20.0	19.7	19.5	-3.4	0.016
Polymer metal complex (Co^{2+})	20.6	20.5	20.3	19.9	19.8	-1.9	0.016

* Solvent was acetone.

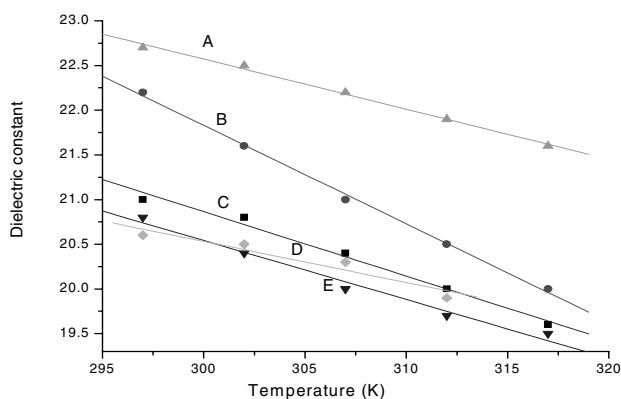


Fig. 6 The curve of dielectric constants vs temperature (A) ▲: end-functionalized PBA; (B) ●: PBA; (C) ■: acetone; (D) ◆: end-functionalized Co^{2+} complex; (E) ▼: end-functionalized Cu^{2+} complex

The negative sign before coefficient should be noticed, which indicates materials own large value of dielectric constant. Moreover, $\text{TK}\epsilon$ of PBA (-0.0049) is much higher than others, It seems dielectric constant of PBA was affected by temperature greatly. But $\text{TK}\epsilon$ of end-functionalized PBA Co^{2+} complex (-0.0019) is contrary. Obviously, polarization ratio of end-functionalized PBA was changed by a small quantity of cations. The intensity of covalent bond of macromolecular ligand was decreased by forming complex bond, which improved the properties of end-functionalized PBA such as dielectric constant. This viewpoint was also proved by the UV and CV spectra.

Conclusions

End-functionalized PBA and its metal complexes have been synthesized and characterized by means of ^1H NMR, GPC, UV, AES, CV and Dielectric Constant. The results show that the end-functionalized PBA possesses strong complex ability and its metal complexes present particular properties such as electrochemical property of metallic ions and dielectric property of PBA. In fact the formation reaction of the complex is completed quickly that indicate the novel end-functionalized PBA may be used as an excellent chelate-extracting agent of metallic ions from solution. Considering the end-functionalized PBA metal complex was composed of polymer and metallic ions novel functional materials may be used as catalyst electrochemical materials and conducting paint, etc.

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