

Polymeric Amines by Chemical Modifications of Alternating Aliphatic Polyketones

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ABSTRACT: Alternating, aliphatic polyketones were chemically modified by using di-amines to obtain polymeric products having pendant amino groups. The used reaction, Paal-Knorr, involves the formation of pyrrole rings along the polyketone backbone. The corresponding kinetics and final conversions are clearly dependent, among others, on statistical factors (two adjacent carbonyls must react in order to obtain ring formation) as well as on the steric hindrance (sterically hindered amino groups

react very slow). The corresponding reaction products (polymeric amines) display very interesting physical properties in aqueous solution. These have been characterized by using dynamic light scattering, Cryo-electron microscopy, fluorescence techniques, etc. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 262–271, 2008

Key words: polyketones; chemical modifications; polymeric amines; functional polymers; Paal-Knorr

INTRODUCTION

Random aliphatic polyketones, produced by the copolymerization of carbon monoxide and olefins, have been known since 1941.¹ Alternating aliphatic polyketones were first reported in 1951.² Since then, significant progress has been made by academia and industry in catalyst and application development.^{3–6} In particular, the synthesis and application development of alternating polyketones has received a lot of attention. This is because the development of highly efficient homogeneous palladium catalyst systems enabled the production of perfectly alternating copolymers of carbon monoxide with olefins and mixtures of olefins. Besides interesting chemical and physical properties, e.g., photodegradability of the virgin polymers,⁷ alternating polyketones can act as excellent precursors for the preparation of functional polymers by chemical modifications. As this type of polyketones contain the recurring highly reactive 1,4 di-carbonyl functionality, the systems can readily be converted into a great variety of functionalized polymers containing pyrrolic, thiophenic, furanic, alcoholic, and phenolic functionalities.^{8–10} The modified polymers, displaying good processability, thermal stability, and electrical properties might well find

wide applications as specialty polymers.^{8–10} Among these modifications, the classic Paal-Knorr reaction, in which the 1,4-dicarbonyl moiety of the polyketones reacts with a primary amine function yielding a pyrrole unit, is one of the dominating reaction routes for the functionalization of alternating polyketones.^{11–14} The poly-pyrrole derivatives exhibited good solubility in common organic solvents and could be utilized as electronic conductors upon doping with iodine.¹⁵ In addition, the pyrrole function is one of the most important heterocycles and the key unit in many biologically active compounds and synthetic pharmaceuticals.¹⁶

The synthesis of polymers containing amine groups has an enhanced interest in recent years due to their potential applications as emulsifiers, drug carriers, DNA-carriers for gene delivery, cation exchange resins, and pharmaceutical uses.^{17–20} However, the high reactivity of the amine groups due to their inherent ability to act as acids, bases, reductants, nucleophiles, or as ligands for transition metals make the preparation of this kind of polymers quite difficult and problematic.²¹ In contrast to a variety of polymerization mechanisms such as anionic, cationic, or radical ones, the route of chemical modifications of polyketones described here just consists of a two component/one-pot reaction without the need of any catalysts and organic solvent using mild conditions during the whole process. It represents a simple, low cost, and straightforward way to prepare polymeric amines. In the present work, we

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report the synthesis of a family of polymeric amines (polyamines) by chemical modifications of alternating polyketones with a set of functional diamines via the Paal-Knorr reaction. The resulting polyamines possess double functionalities: the N-substituted 2,5-pyrrole-diyl group incorporated in the polymer backbone and a substituent containing an amino functionality, which can be either primary, secondary, or tertiary and both aliphatic or aromatic. The factors affecting the chemical reactivity of the polyketones with the diamines such as reaction conditions (time, temperature, initial molar ratio between amino groups of the diamines and 1,4 arrangement of di-carbonyl groups on the polyketones), ethene content of the polyketones, and the chemical structure of the diamines were thoroughly studied. The polyamines are expected to transform into water-soluble cationic species by the simple protonation with weak acid or by the quaternization of the amino groups. Thus physical properties of the polyamines as water dispersion were characterized by a combination of static and dynamic light scattering, surface tension, and Cryo-transmission electron microscopy (Cryo-TEM). Furthermore, as aromatic rings (pyrroles) are present in the backbone of the polymer, a study of the fluorescence property of the polyamines was carried out in water solution.

EXPERIMENTAL

Materials

The alternating polyketones with 0% ethene (PK0, M_w 1680), 30% ethene (PK30, M_w 3970), and 50% ethene (PK50, M_w 5350) based on the total olefin content were synthesized according to a reported procedure.²² 1,2-Diaminopropane (1,2-DAP, Acros), 1,3-Diaminopentane (1,3-DAPe, Aldrich), 2-(Dimethylamino)ethylamine (2-DAEA, Aldrich), 2-Diethylaminoethylamine (2-DEAEA, Aldrich), 4-Picolylamine (4-PcA, Aldrich), 2,5-Hexanedione (Acros), Acetic acid (Acros), Iodomethane (Aldrich), and Tetrahydrofuran (THF, Acros) were purchased and used as received.

Model component reaction

2,5-Hexanedione (34.9 mg, 0.31 mmol) was added to 1,2-Diaminopropane (25.6 mg, 0.35 mmol) in 0.7 mL of $CDCl_3$. The resulting mixture was shaken for a few minutes and transferred into an NMR tube (5 mm in diameter). The progress of the reaction was monitored with 1H NMR spectroscopy at 50°C for 11.25 h. The spectra were recorded at regular time intervals of 25 min.

Chemical modification of the polyketones

The chemical modifications were carried out in a sealed 250 mL round bottom glass reactor with a reflux condenser, a U-type anchor impeller, and an oil bath for heating. After the polyketones were preheated to the liquid state at the employed reaction temperature (80–100°C), the diamines were added dropwise into the reactor in the first 20 min. The stirring speed was set at a constant speed of 500 rpm. During the reaction, the mixture of the reactants changed from the slight yellowish, low viscous state into a highly viscous brown homogeneous paste. The reaction rate was monitored using potentiometric titrations. After the reactions completed and the polymers cooled down to room temperature, the products derived from the 1,2-DAP and 4-PcA changed into rigid solid material, while the other products appeared as waxy or soft materials. The resulting polyamines were washed several times with deionized Milli-Q water. After filtering and freeze-drying, light brown polymers were obtained as the final products.

Preparation of the polymer solutions

The polyamines as such were not soluble in water. However, they display good solubility in acidic water. Accordingly, 100 mg/mL stock solutions of PK30 modified with 1,2-DAP and 1,3-DAPe in deionized Milli-Q water were prepared by adding the appropriate amount of acetic acid solution to match a desired protonation level and stirring with a magnetic stirbar at 80°C for 1.5 h. The tertiary amino groups of PK50 modified with 2-DAEA, 2-DEAEA, and 4-PcA, and PK30 modified with 4-PcA were quaternized by treating the polymers with a 10 molar excess of methyl iodide over the amino groups in THF at room temperature for 24 h. The solvent and excess methyl iodide were removed under reduced pressure. The 10 mg/mL stock solutions of the quaternized polymers were prepared in the deionized Milli-Q water by stirring with a magnetic stirbar at 80°C for 1 h and then passing through 200 nm syringe filters after complete dissolution. All the solutions were equilibrated overnight before measurements were performed.

Nuclear magnetic resonance and FTIR spectroscopy

1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer using $CDCl_3$ as a solvent. The FTIR spectroscopy was performed using Perkin-Elmer Spectrum 2000 and spectra of the polymers were carried out using KBr pellets.

Potentiometric titrations

Potentiometric titrations were performed at room temperature for determination of the amine number of the modified polyketones using a titrator (702 SM Titrino, Metrohm) with an automatic burette of 10 mL capacity. A perchloric acid (HClO₄) (0.1M) solution in water, standardized by potassium hydrogen phthalate, was used as the titrating agent. A THF/water (9 : 1) mixture, able to solubilize the polyamines at all protonation levels (i.e., during the all titration), was used as titration solvent (120 mL) for the samples (0.2–0.3 g). The inflection point was identified from the titration curve. Three or four measurements were performed for each sample. The average amine number was taken and the obtained standard error of the average value was less than 1%. The conversion rates of the diamines, C_{amine} , and carbonyl groups of the polyketones, C_{CO} , were determined by the following formulas:

$$C_{\text{amine}} = (A_i - A_f)/A \times 100\% \quad (1)$$

$$C_{\text{CO}} = C_{\text{amine}} \times I_{\text{am/CO}} \times 100\% \quad (2)$$

where A_i is the amine number before the modification, A_f is the amine number after the modification, A is the standard amine number for 100% conversion rate, $I_{\text{amine/CO}}$ is the initial reaction molar ratio between the diamines and 1,4-arrangement of di-carbonyl groups of the polyketones.

Static and dynamic light scattering

The static and dynamic light scattering (SLS and DLS) measurements were performed on a Zetasizer 5000 instrument (Malvern Instruments, UK) at a wavelength of 633 nm and at a temperature of 25°C. Scattered light was detected at a 90° angle. The viscosity of (0.89 mPa s) and the refractive index (1.33) of water at 25°C were used for data analysis. The intensity autocorrelation functions obtained from the DLS were analyzed using CONTIN algorithm in all the measurements. The apparent hydrodynamic diameter, D_H was obtained by using the Stokes-Einstein equation:

$$D_0 = kT/3\pi\eta D_H \quad (3)$$

where D_0 is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solution.

Drop tensiometry

Surface tension measurements on the polymer solutions were performed using a drop tensiometer (Lauda, TVT-1), with a Lauda RM6 temperature con-

troller. The temperature was controlled at (25 ± 0.1)°C during the period of measurements. The inner radius of the steel capillary was 1.055 mm and the employed syringe had a volume of 500 μL. The surface tension value for deionized Milli-Q water (70 mN/m) was taken as an internal standard before starting measurements. The error given by the instrument was less than 0.1 mN/m.

Cryo-transmission electron microscopy

A drop of the polymer solution was deposited on a glow discharged carbon-coated grid. After blotting away the excess of solution with filter paper, the grids were rapidly plunged into liquid ethane. The frozen specimen was transferred to a Gatan (model 626) cryo-stage and examined in a Philips CM 120 cryo-electron microscope operating at 120 kV. Micrographs were recorded under low-dose conditions at about –170°C.

Fluorescence spectroscopy

The fluorescence measurements were performed on a Fluorolog 3-22 spectrofluorimeter. The spectra were recorded between 365 nm and 650 nm with the excitation wavelength of 350 nm. The slit width of the emission was kept at 1 nm step size. All the measurements were performed in the de-ionized Milli-Q water at room temperature.

RESULTS AND DISCUSSION

Modifications of the polyketones

The current study was focused on a new class of the polyketones (M_w 1500–5000), alternating co- and terpolymers of carbon monoxide, ethane, and propene (Fig. 1) as starting materials for modifications. Depending on the molar ratio of ethene and propene, the consistency of this type of polyketones varies from viscous flowing materials at room temperature for ethene free materials to waxy or melting solids at 50% ethene based on the total olefin content. The chemical reactivity of polyketones with different kinds of diamines using potentiometric titrations have been systematically investigated here (Fig. 2). Although the exact mechanism of the reaction and in particular the order by which the addition/elimination steps take place has not yet been identi-

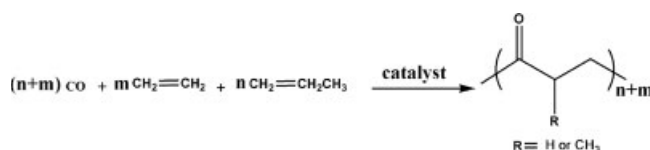


Figure 1 Synthesis of CO-ethene-propene based low molecular weight polyketones.

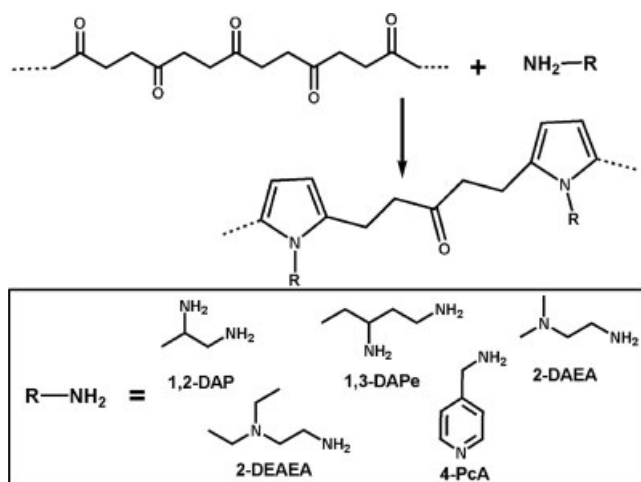


Figure 2 Scheme of the reaction between polyketones and functional diamines.

fied, the chemical characterization of the final stable product has been well established.^{9–14} The presence of pyrrole rings in the backbone of the polymeric amines has been confirmed by FT-IR and NMR analysis of all our reaction products. Typical is the appearance, after the reaction, of FT-IR absorption peaks around 3100 cm^{-1} (assigned to the C–H stretching vibration of the pyrrole rings), of ^1H NMR peaks around 6 ppm (assigned to the protons attached to the pyrrole rings) and ^{13}C NMR peaks at around 130 ppm (assigned to the C-atoms of the pyrrole rings).

Since the use of polyketones as such, due to the polymeric nature of the substrate, resulted in low resolution spectra, we determined the exact chemical structure of the product by using model compounds. In particular, we carried out the reaction between 1,2-DAP and 2,5-hexanedione in an NMR tube in CDCl_3 . The NMR spectra of the starting reaction mixtures and after 11.25 h reaction time are reported in Figure 3(a). The appearance of the pyrrole ring absorptions at about 5.7 ppm, of the $-\text{CH}_2-$ groups attached to the pyrrole ring (3.6 ppm) and of the $>\text{CH}-$ in β -position with respect to the pyrrole rings (3.2 ppm) all testify the formation of the reported product. Moreover, from the ratio of peaks at 1 ppm (methyl group of the reacted 1,2-DAP) and at 0.95 ppm (methyl groups of unreacted 1,2-DAP), it is possible to calculate the conversion at a given time [Fig. 3(b)]. It is clear that the reaction at 50°C is actually slow, reaching a diamine conversion of 80% in 11.25 h. On the other hand, by comparison with the ^1H NMR spectra, it can also be seen that only the less hindered amino group actually reacts with the carbonyl moieties, the other one remaining pendant from the pyrrole ring in agreement with what is reported in previous studies.²³

With the information given by the model compound reaction, we then set up a more detailed study for the polymeric systems by carrying out reactions under several different experimental conditions. We first investigated the kinetics of the reaction under mild condition (50°C) by determining and calculating the diamine conversion as function of time (Fig. 4). An initial molar ratio ($I_{\text{am/CO}}$) of 1 between the 1,2-DAP and 1,4 arrangement of di-carbonyl groups on the PK30 were employed. Because of the steric effect of the 1,2-DAP, only the nonsterically hindered amino group (position 1 in 1,2-DAP) could react with 1,4-di-carbonyl unit and led to the desired regiospecific reaction. The other one (position 2 in 1,2-DAP) remains intact as functional group. This is consistent with the results of the model component reactions between 2,5-hexanedione and diamines with steric hindrance²³ and to our own data reported above. It is possible to observe how the conversion increases logarithmically with the reaction time. After about 4 h the conversion reaches

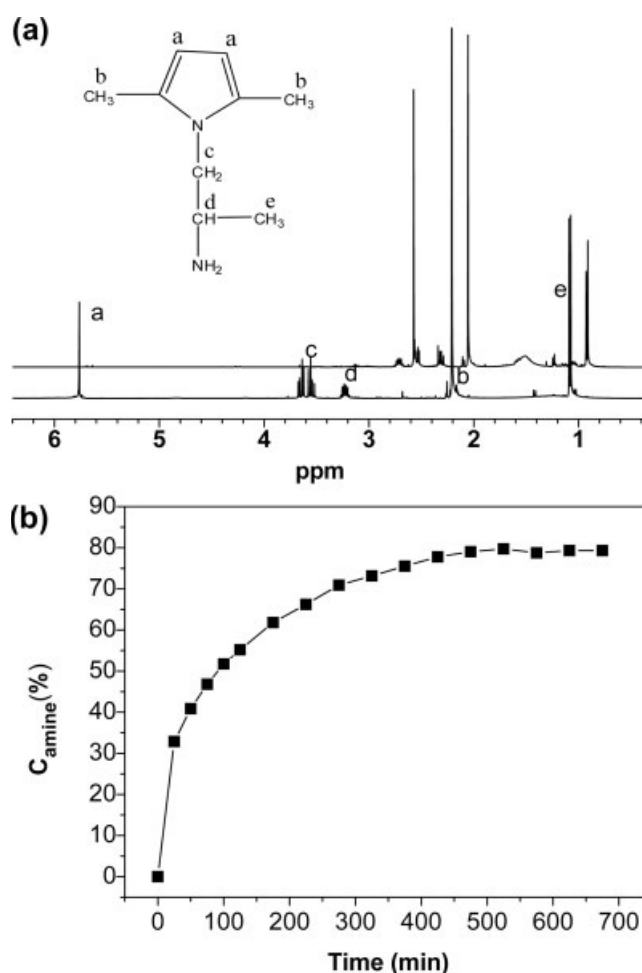


Figure 3 Model compounds reactions (a) ^1H NMR spectra before reaction (upper spectrum) and after 11.25 h (lower spectrum); (b) reaction kinetics, determined by ^1H NMR.

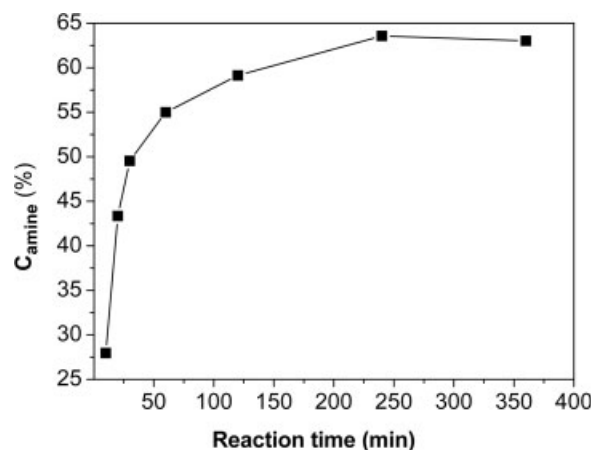


Figure 4 Diamine conversion rate as function of time in the reaction of PK30 with 1,2-DAP.

a steady value of about 65%. The fact that not all amino groups are actually consumed in the reaction, i.e., conversion never reaches 100% for an initial equimolar ratio, is easy to understand, if one considers that every amino groups must react with two adjacent carbonyl groups to yield the final pyrrole. Statistically, however, there exists always the chance that two different amino groups will react and result, after ring closure, in two pyrroles separated by a single carbonyl group. In this case, no further reaction is available with another amino group, thus preventing the conversion to reach 100% for the initial equimolar ratio.

The situation changes when using a different $I_{am/CO}$ (Table I) at 80°C after 240 min of reaction time. The diamine conversion steadily decreases with the amount of the same reactant present originally in the reaction mixture. Moreover, conversions very close to 100% are observed when using an $I_{am/CO}$ of about 1.0 : 0.6 (0.7). The latter clearly confirms that the limitation in the conversion is not due to the amine reactivity but to the statistical restraint mentioned above. Moreover, from a practical point of view, the same fact indicates that a maximum of about 60–70% of the carbonyl groups can actually react with the amino groups due to the availability of the 1,4-di-carbonyl groups. The reaction temperature has very little impact on the conversion between 80°C and 100°C (Table II), at least if compared with the influence of the composition. Between 80°C and 100°C the diamine and carbonyl conversion remains basically unaffected at $I_{am/CO} = 1 : 0.6$ while it increases slightly at $I_{am/CO} = 1 : 0.8$. These data indicate once more that there is a maximum to the amine amount able to react with the PK30, corresponding to around 70% of the carbonyl groups. At the same time, the conversion might be improved more, when working in excess of diamine with

TABLE I
Conversion of Diamine and Carbonyl Groups in the Reaction of PK30 with 1,2-DAP as a Function of $I_{am/CO}$ at 50°C

$I_{am/CO}$ (mol : mol)	C_{amine} (%)	C_{CO} (%)
1 : 0.6	99	59
1 : 0.7	92	64
1 : 0.8	83	67

respect to the 70% of carbonyl groups as mentioned earlier, by increasing the reaction temperature.

We finally investigated the effect of the chemical structure of the diamine and the polyketones on the conversion (Table III). All the reactions proceeded exceedingly well except for the crosslinking of PK50 with 1,2-DAP and 1,3-DAPe. No crosslinking can occur for the PK50 with 2-DAEA, 2-DEAEA, 4-PcA due to the fact that only primary amino groups are reactive in the Paal-Knorr reaction. Because of the steric hindrance, only one amino group of 1,3-DAPe could react with PK0 and PK30, a very similar effect to the one of the 1,2-DAP. The conversion rate of different diamines is found to be quite comparable with each other. All resulting polyamines can be readily dissolved into common organic solvents, such as methanol, ethanol, THF, and chloroform. In contrast, virgin polyketone oligomers (before modification) are only slightly soluble in protic solvents such as methanol and ethanol. Conversion increases with increasing ethene content of the polyketones, in particular this leads for 1,2-DAP, 1,3-DAPe to crosslinking when using PK50. It is interesting to note that the diamine conversion rate with PK50 can even reach almost 100%, which corresponds to around 80% carbonyl group usage. This trend could be either due to a different solubility of the different diamines in the molten polyketones or to the higher reactivity at high ethene content because of the lower steric hindrance of the carbonyl groups of PK50. However, a closer look at the value of the solubility parameters²⁴ for every possible couple of polyketones and diamines shows that there is no real correlation between solubility (estimated as absolute value of the solubility parameter difference) and conversion (Fig. 5). As a consequence, like already

TABLE II
Conversion of 1,2-DAP and Carbonyl Groups as Functions of Temperature and $I_{am/CO}$ for the Reaction with PK30

$I_{am/CO}$ (mol : mol)	T (°C)	C_{amine} (%)	C_{CO} (%)
1 : 0.6	80	99	59
1 : 0.6	100	99	59
1 : 0.8	80	83	67
1 : 0.8	100	90	72

TABLE III
Conversion of Diamine and Carbonyl Groups as Functions of the Kind of Polyketone and Diamine ($I_{\text{am/CO}} = 1 : 0.8$, $T = 100^\circ\text{C}$, $t = 240$ min)

Diamine	PK0		PK30		PK50	
	C_{amine} (%)	C_{CO} (%)	C_{amine} (%)	C_{CO} (%)	C_{amine} (%)	C_{CO} (%)
1,2-DAP	80	64	90	72	Crosslinking	
1,3-DAPe	81	65	82	65	Crosslinking	
2-DAEA	76	61	82	66	94	76
2-DEAEA	71	57	76	61	98	78
4-PcA	74	60	77	61	99	79

stated in the literature,^{9,10} we must conclude that the steric effect plays a major role here.

Characterization of the polymeric amines

Next, the synthesized polymeric amines were protonated with the use of a weak acid-acetic acid (Fig. 6) and successively dispersed in water. We first investigated the influence of the protonation level on the particle dimension of the resulting dispersion of PK30 modified with 1,2-DAP [Fig. 7(a)]. Below 35% protonation level, the polymer is insoluble in water and precipitate. In first instance, it must be noticed how the particle size decreases quite significantly with the protonation level. This is most probably related to the stabilization effect, which prevents coagulation, due to the positive charges at the interface between the particles and water according to the well-established DLVO theory.²⁵ A confirmation of this hypothesis is given by the observed salt effect that addition of NaCl (150 mM) to the dispersion results in a screening of the electrostatic repulsion between particles and therefore in an increased average particle size. The salt effect is rather pronounced at low protonation level. Within the protonation

level range from 35% to 45%, the addition of the salt leads to the flocculation (salted out) of the polyamines in the solution. The protonation level affects the particle size but has no remarkable influence on the width of the distribution [Fig. 7(b)], which remains basically monomodal at all protonation levels. Moreover, the repulsive electrostatic interaction is strong enough to stabilize the corresponding dispersion even after 1 month [Fig. 7(a)] at room temperature. The same lack of effect is observed when comparing the scattering intensity, which corresponds to the number of the particles in the solution, as function of protonation level and time [Fig. 7(c)]. The increase of the protonation level makes the polymers more hydrophilic and keen to molecularly dissolve into water, thus leading to a decrease of the scattering intensity. A very weak scattering intensity can be observed with further increasing the protonation level above 60%, indicating that the polymers are able to behave like polyelectrolytes and become water soluble.

A deeper insight into the particle size and in general the morphology of the dispersions was obtained by using Cryo-TEM (Fig. 8). It is clear how the average particle size decreases with the protonation level, in striking agreement, also from a quantitative point of view, with the light scattering measurements. In this respect such dispersions could rightly be called "nano," starting with an average dimensions of about 50 nm for the spherical polymer micelles at 40% protonation level and ending up with an average of even less than 10 nm at 100% protonation level. Such outstanding uniformity of the dispersions as well as their stability with respect to time has of course nice and important consequences for the application of such dispersions. One factor that may remarkably affect both particle size and

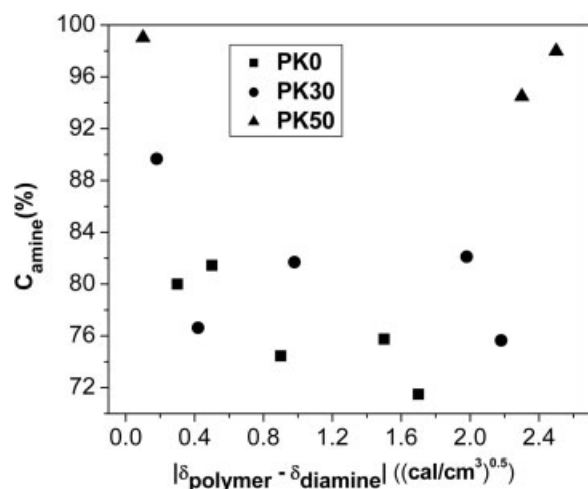


Figure 5 Effect of the difference of solubility parameters between the polyketones and diamine on the conversion rate of the diamines.

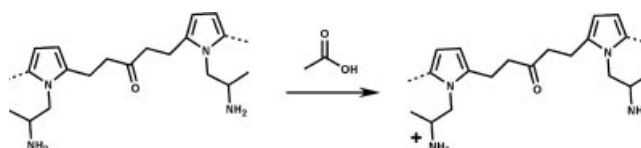


Figure 6 Protonation of polyamines with acetic acid (only derivatives of 1,2-DAP is shown for brevity).

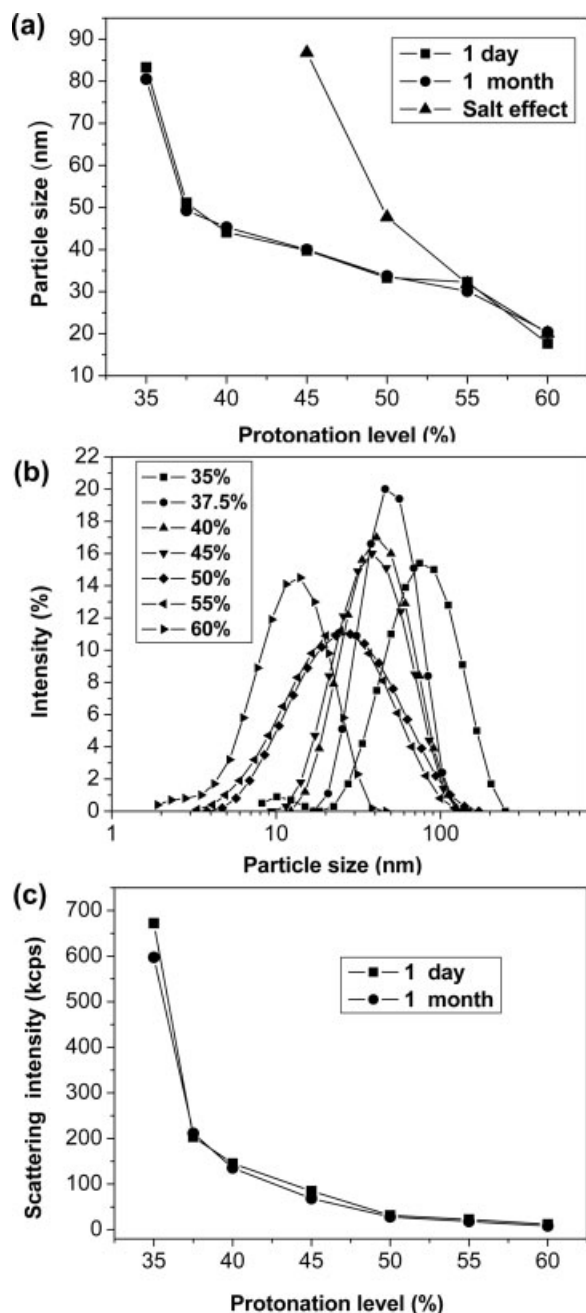


Figure 7 Influence of protonation level on (a) particle size; (b) particle size distribution; (c) scattering intensity for PK30 modified with 1,2-DAP (5 mg/mL) in water.

the light scattering intensity of the dispersions is the pH drop caused by the addition of the strong acid (0.5M HCl) (Fig. 9), which may provide the information for the further application as drug carriers.²⁶ For a derivative of PK30 with 1,2-DAP at 40% protonation level, it is found that once the micelles are formed, the micelle size does not strongly depend on the pH drop even after 1 day and 3 days time-period. However, the considerable decrease of the scattering intensity indicates very fast kinetic for the micelles into unimers, corresponding to deeply pro-

tonation of amino groups, once the pH drop is made.

The fact that the modified PK30 has a surfactant-like structure or amphiphilic character is not only testified by its chemical structure but also by the measurement of surface tension of the resulting dis-

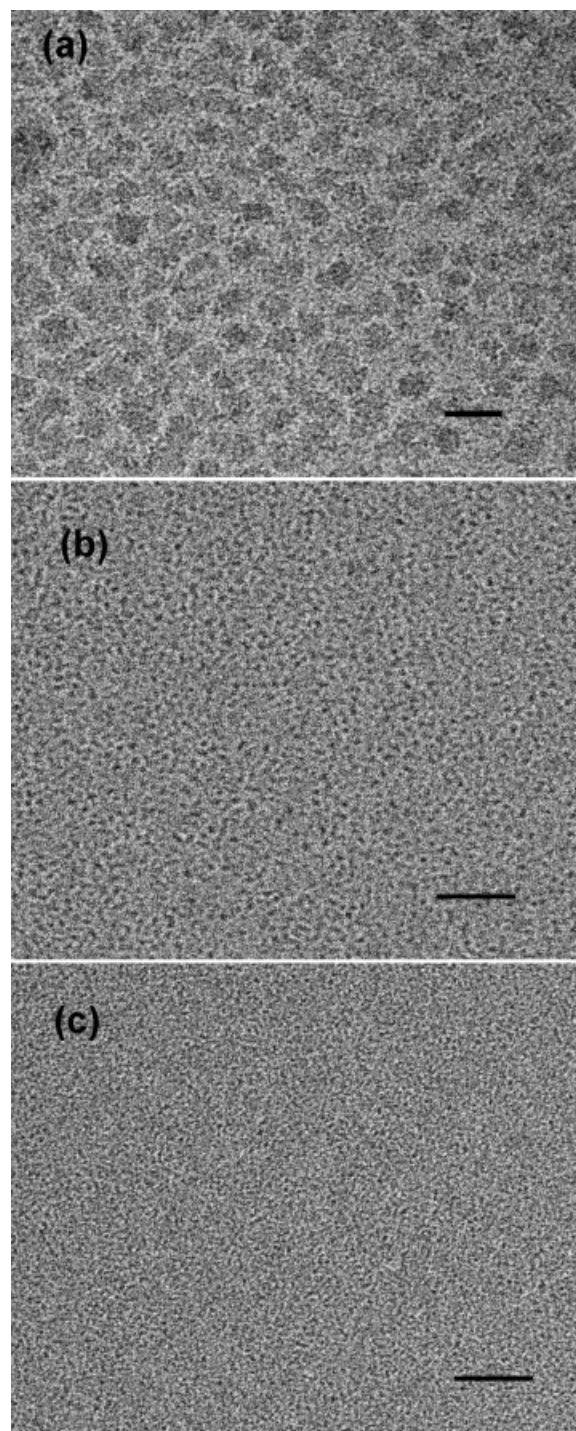


Figure 8 Cryo-TEM images of PK30 modified with 1,2-DAP dispersed in water at (a) 40% protonation level; (b) 60% protonation level; (c) 100% protonation level. Bar represents 50 nm.

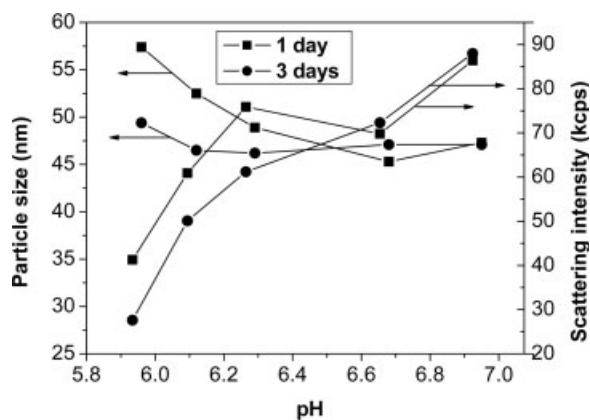


Figure 9 Influence of pH drop on the particle size and scattering intensity of PK30 modified with 1,2-DAP (2 mg/mL).

persions as a function of the concentration and protonation level of the polyamines (Fig. 10). Surface tension, indicating the adsorption of the surfactants at the air–water interface, decreases as expected with the concentration of the polyamines and with the protonation level. The latter effect is probably related to the more hydrophobic nature of the modified PK30 with decreasing protonation level, which thus determines its surface activity. This phenomenon is similar to some other synthetic block copolymers with a hydrophilic–hydrophobic balance.²⁷ Surface tension measurements result in a relatively smooth curve due to molecular weight distributions of polymer, a clear difference with low molecular weight surfactants and thus there is no well-defined critical micelle concentration (CMC) that could be identified.²⁸

Aqueous properties were also studied on the PK30 with 1,3-DAPe (Table IV and Fig. 11) at two different protonation levels. A very similar aqueous behavior to the one displayed by PK30 modified with 1,2-

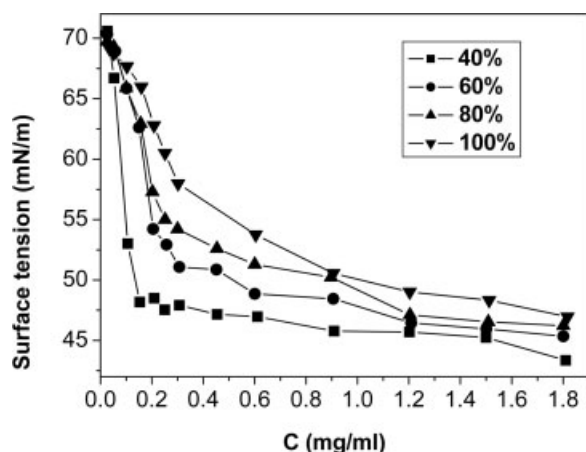


Figure 10 Surface tension of PK30 modified with 1,2-DAP as function of protonation level and concentration.

TABLE IV
Influence of the Protonation Level on the Particle Size and Scattering Intensity of PK30 Modified with 1,3-DAPe

Protonation level (%)	Particle size (nm)	Scattering intensity (kcps)
70 (1 day)	302	425
70 (2 weeks)	295	350
70 (salt effect)	264	410
80 (1 day)	296	163
80 (2 weeks)	265	190
80 (salt effect)	263	176

DAP can be observed. Partial protonation of the amine groups on the PK30 with 1,3-DAPe induces larger, loose aggregates with an average particle size around 300 nm, compared with an average particle size of less than 50 nm for PK30 with 1,2-DAP. This may be correlated with the difference in chemical structure of the used diamines for modification, which thus leads to the diversity of the aqueous properties. The polymer solutions display good stability during the 2 weeks of measurement time. The salt effect (150 mM NaCl) here is not as much pronounced as for PK30 with 1,2-DAP. In terms of surface activity, it can be seen in Figure 11 that the surface tension decreases with an increase in the concentration and, as expected, low protonation levels result in a higher surface activity.

The solution behavior of the modified polymer after methylation was also studied by measuring the surface tension (Fig. 12). The surface tension of the modified PK50 with 2-DAEA, 2-DEAEA, 4-PcA, and after methylation decreases in a less dramatic manner to a limited value around 65–67 mN/m with an increase in polymer concentration. This may be explained by the fact that the modified PK50 after the methylation has a high content of the ionized amino groups around the backbone, leading to the

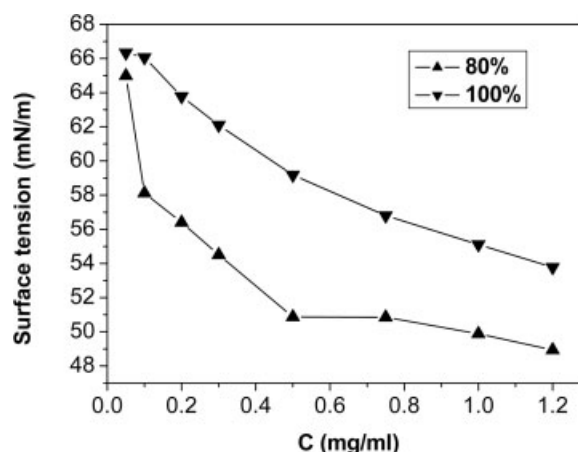


Figure 11 Surface tension of PK30 modified with 1,3-DAPe as function of protonation level and concentration.

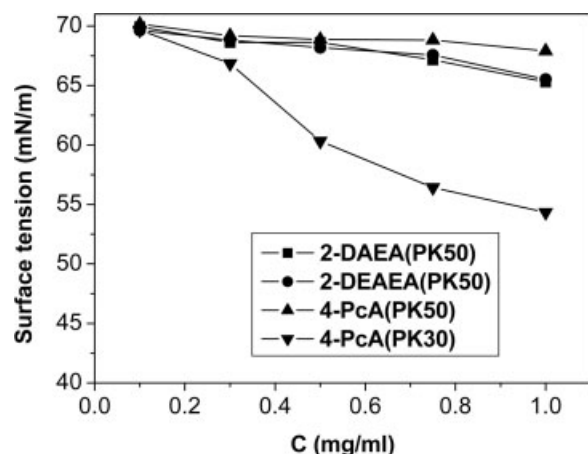


Figure 12 Surface activity measurements for water dispersion of PK50 modified with 2-DAEA, 2-DEAEA, 4-PcA, and PK30 modified 4-PcA.

enhanced hydrophilicity. Thus the polymers become water-soluble cationic polyelectrolytes. This is also confirmed by the fact that there are no small aggregates formed even at the high polymer concentration (10 mg/mL). It is worth to note that the observed difference in surface activity for the modified PK30 and PK50 with 4-PcA might be due to the increasing conversion rate of the diamines from the 77% to 99% and to the different molecular weight of the polyketones. Indeed, we already showed and discussed above (Fig. 10) how the protonation level (i.e., the hydrophilicity of the polymer) negatively affects the surface activity. In the present case, one might notice that higher conversion rate for 4-PcA (as in the case of the reaction with PK50 compared with PK30) results in a stronger hydrophilic character of the polyamine (simply more hydrophilic groups are grafted along the backbone) and thus, in agreement with the concept expressed above, also in lower surface activity.

All synthesized polymers behaved like intrinsically photoluminescent materials and could display fluorescent properties, which can be attributed to the multiple aromatic pyrrole rings in the backbone. For example, the fluorescent spectra of PK30 modified with 1,2-DAP at the 100% protonation and with 4-PcA after methylation are shown in Figure 13. In aqueous solution, the fluorescent spectra show maxima at around 420–430 nm for PK30 with 1,2-DAP and around 470 nm for the PK30 with 4-PcA. A small red shift of the fluorescence emission for PK30 with 1,2-DAP takes place with an increase of concentration. The different maximum emission between these two polyamines can be attributed to their different chemical structure. The fluorescence intensity increases with increasing the initial polymer concentrations. After reaching the maximum, the fluorescence intensity decreases with further increasing the

concentration. This behavior is most probably due to a self-quenching effect.²⁹

The aqueous properties described above are very important when considering the possible applications of the synthesized polyamines. Indeed their surface activity strongly suggest a possible use as surfactants (for example in the dispersion of virgin polyketones in water). The latter has been already reported in the literature¹⁴ and it is the object of a systematic study presently carried out in our group. Moreover, the simple presence of ammonium groups, whose amount is easily tunable by controlling the protonation reaction, suggests the use of these polymers as cationic ones in the formation of complexes with polyanions (e.g., DNA, polyacrylic acid, etc.). Such complexes are currently under investigation in our group as they might promote the use of these materials for biomedical applications.

CONCLUSIONS

A series of new polymeric amines were prepared by chemical modifications of low molecular weight

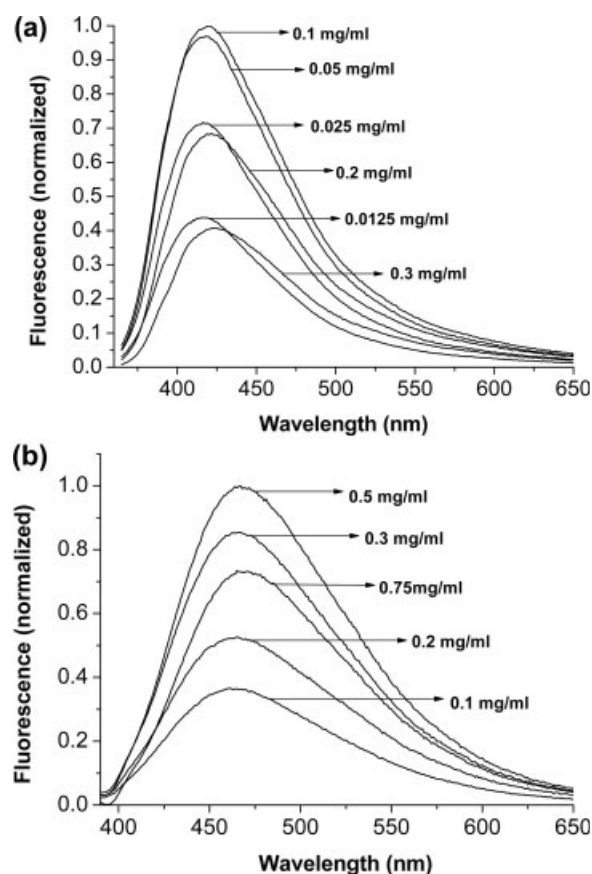


Figure 13 Normalized fluorescence intensity of (a) PK30 modified with 1,2-DAP; (b) PK30 modified with 4-PcA in water at a function of concentration.

alternating polyketones with different kinds of diamines. It was found that the rate of reaction strongly depends on the steric hindrance introduced into the reactants. During the reaction, around 70–80% of carbonyl groups of the polyketones could be converted into pyrrole units in the backbone. It is demonstrated that the resulting polymers, after protonation or alkylation of the amino groups, display interesting aqueous solution behavior. Indeed they act as polymeric surfactants or polyelectrolytes. Furthermore, they exhibit fluorescence in aqueous solution, which may be promising for use as water-soluble fluorescence probes.

References

1. Ballauf, F.; Bayer, O.; Teichmann, L. DE. Pat. 863,711 (1941).
2. Reppe, W.; Magin, A. U.S. Pat. 2,577,208 (1951).
3. Drent, E.; Budzelaar, P. H. M. *Chem Rev* 1996, 96, 663.
4. Sommazzi, A.; Garbassi, F. *Prog Polym Sci* 1997, 22, 1547.
5. Bianchini, C.; Meli, A. *Coord Chem Rev* 2002, 225, 35.
6. Durand, J.; Milani, B. *Coord Chem Rev* 2006, 250, 542.
7. Sen, A. *Acc Chem Res* 1993, 26, 303.
8. Jiang, Z.; Sangneria, S.; Sen, A. *J Polym Sci Part A: Polym Chem* 1994, 32, 841.
9. Chen, J.; Yeh, Y.; Sen, A. *Chem Commun* 1989, 965.
10. Sen, A.; Jiang, Z.; Chen, J. *Macromolecules* 1989, 22, 2012.
11. Kiovsky, T. E.; Kromer R. C. U.S. Pat. 3,979,374 (1976).
12. Brown, S. L. U.S. Pat. 5,081,207 (1992).
13. Sinai-Zingde, G. D. U.S. Pat. 5,605,988 (1997).
14. Broekhuis, A. A.; Freriks, J. U.S. Pat. 5,952,459 (1999).
15. Jiang, Z.; Sen, A. *Macromolecules* 1992, 25, 880.
16. Jones, R. A. *Pyrroles*; Wiley: New York, 1990.
17. Butun, V.; Liu, S.; Weaver, J. V. M.; Bories-Azeau, X.; Cai, Y.; Armes, S. P. *React Polym* 2006, 66, 157.
18. Gil, E. S.; Hudson, S. M. *Prog Polym Sci* 2004, 29, 1173.
19. Aoyama, Y.; Novak, B. M. *Macromolecules* 2001, 34, 6842.
20. Smedt, S. C. D.; Demeester, J.; Hennink, W. E. *Pharmacol Res* 2000, 17, 113.
21. March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992.
22. Drent, E.; Keijsper, J. J. U.S. Pat. 5,225,523 (1993).
23. Kostyanovsky, R. G.; Kadorkina, G. K.; Mkhitarian, A. G.; Chervin, I. I.; Allev, A. E. *Mendeleev Commun* 1993, 21.
24. Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic: Lancaster, 1991.
25. Stokes, R. J.; Evans, D. F. *Fundamentals of Interfacial Engineering*; Wiley: New York, 1997.
26. Gillies, E. R.; Frechet, J. M. J. *Chem Commun* 2003, 1640.
27. De Paz-Banez, M. V.; Robinson, K. L.; Vamvakaki, M.; Lascelles, S. F.; Armes, S. P. *Polymer* 2000, 41, 8501.
28. Butun, V.; Armes, S. P.; Billingham, N. C.; Tuzar, Z.; Rankin, A.; Eastoe, J.; Heenan, R. K. *Macromolecules* 2001, 34, 1503.
29. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum: New York, 1999.