Polyelectrolytes from NS-Novolak Production Waste

Wioletta M. Bajdur,[1] Wiesław W. Sułkowski[2]

[1]*Department of Ergonomics and Work Protection, Technical University of Częstochowa, Armii Krajowej 36B, 42-200 Częstochowa, Poland*
[2]*Department of Environmental Chemistry and Technology, Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland*

Received 5 June 2002; accepted 5 November 2002

ABSTRACT: The chemical modification of polymer plastic wastes into useful products, such as polyelectrolytes, could be a step toward their management. For these products to be obtained, the synthesis of amino derivatives of phenol-formaldehyde resin (NS-novolak) production waste by means of known methods was performed. Products that contained different contents of amino groups in the polymer chains and that were soluble in dilute KOH and NaOH solutions were obtained. The flocculation properties of these products were tested. Studies were conducted of mine water from the Kleofas coal mine and for water from the Częstochowa metallurgical plant blast-furnace circulation system. The amino derivatives of the phenol-formaldehyde resin waste were found to have good flocculation properties. The application of these products caused a decrease in the turbidity and concentration of the dissolved contamination and improved the quality parameters of the purified sewage. These polyelectrolytes could also be used in industrial water treatment. J Appl Polym Sci 89: 3000–3005, 2003

Key words: polyelectrolytes; functionalization of polymers; resins; waste; recycling

INTRODUCTION

Polymer plastic wastes from packing materials of low density and, therefore, high capacity are the main source of solid wastes in waste dumps.[1] Waste from phenol-formaldehyde resin production is also a problem. The elaboration of a polymer plastic waste management technology or a technology of its recycling is very important from an economic point of view. This could help to lower the hazard to the environment. The chemical modification of polymer plastic wastes into sorbents or polyelectrolytes could be a way of managing them. This would make it possible to reduce the amount of dumped waste and to produce sorbents or polyelectrolytes. Moreover, it would allow for effective sewage and water treatment.[2,3] Low effective concentrations of polyelectrolytes are not hazardous to the environment, even if they are dumped with sewage sludge in a waste dump. Studies on the synthesis of polyelectrolytes from expanded polystyrene wastes and from phenol-formaldehyde resins have confirmed their efficacy.[4–8] These studies are now particularly important because the concentrations of organic compounds, nitrogen and sulfur compounds, and heavy metals in water and sewage are constantly increasing. Recently, new simultaneous technologies using chemical and biological treatments have been used in sewage treatment processes to improve the quality of purified water. The chemical treatment of sewage increases the amount of insoluble impurities (in a different state of dispersion) extracted from the sewage. Coagulation is a complex and not ideal process. It depends on many parameters, such as the physicochemical composition and temperature of water, the kind and dose of the coagulant, and the hydraulic parameter of the process. Studies on increasing coagulation efficacy have also been conducted.[8,9] Recently, the precipitation process of impurities with coagulants has been enhanced with small amounts of anionic polymer flocculants (anionic polyelectrolytes). The syntheses of flocculants are oriented to an increase in the ionic group content in one chain polymer exhibiting a high molecular weight. The interactions between small particles and polymer molecules are important in the purification of water and sewage and in other applications. The first flocculation mechanism was proposed 20 years ago. A number of models of the adsorption of polymer molecules onto small particles and the flocculation and stabilization processes of fine suspensions have also been proposed.[10–23] The main mechanisms for the destabilization of particles by charged polymers are bridging and mosaic flocculation and charge neutralization. In bridging flocculation, one polymer chain adsorbs onto two or more particles simultaneously. In mosaic flocculation, in which, for example, positively charged polymers adsorb onto negatively charged particles,

Correspondence to: W. W. Sułkowski (wsulkows@uranos.cto.us.edu.pl).

Journal of Applied Polymer Science, Vol. 89, 3000–3005 (2003)

locally positive patches on the particles may be formed. In charge neutralization, in which charged polyelectrolytes adsorb onto an oppositely charged surface, the surface charge is nearly compensated. Bridging flocculation and mosaic flocculation take place when the surface is not yet completely covered, that is, when the polymer concentration is low, or in the initial stage of the adsorption process. Because these processes may take place immediately after the addition of the polymer, they depend very much on the mixing conditions. Charge neutralization may take place both at low and high coverage, depending on the surface charge density and polymer charge. Models for dual-polymer and microparticle systems have been discussed too. It is thought that the flocculation process in the presence of nonionic and ionic flocculants runs in different ways. Despite many reports on the flocculation mechanism, studies of this mechanism for phenol-formaldehyde resin derivatives have not been conducted. Therefore, the synthesis of polyelectrolytes, the study of these processes, and the study of the physicochemical and flocculation properties of these compounds are quite significant. The great diversification in the properties of water dispersion systems (sewage) and the variety of technological treatment processes in which flocculants are used require flocculants with different properties.[24,25] The polymer flocculation efficiency depends on the types of functional groups and their arrangement in a polymer chain and on the polymer properties, the polymer chain hydrophobicity, the average molecular weights, the macromolecular parameters in solution, the amount of the polymer, and the polymer concentration in solution. The determination of these parameters is crucial for determining the usability of synthesized organic polymers as polyelectrolytes. However, the producers of polyelectrolytes limit the parameters only to the polymer type and its dose for a specific water quality, and the usability of the polyelectrolyte for a specific type of water is confirmed under service conditions.

In conclusion, the modification of polymer plastic wastes into polyelectrolytes could be an appropriate way of increasing the efficiency of sewage treatment processes, limiting the energy consumption of these processes, and managing polymer plastic wastes and their recycling. The synthesis of NS novolak amino derivatives was performed to obtain these polyelectrolytes.

EXPERIMENTAL

NS novolak waste from the ERG plastic factory (Pustków, Poland) and nitric acid, sulfuric acid, hydrochloric acid, calcium carbonate, sodium carbonate, ammonia, stannic chloride, and silver sulfate from POCh (Gliwice, Poland) were used for chemical modification. Aluminum sulfate (POCh), which was used as a coagulant (1% solution), a commercial polyelectrolyte named Praestol 2515 (an anionic commercial polyelectrolyte synthesized from polyacrylamide), Jaroszów clay, which was used for the preparation of high-turbidity water according to the PN-71/C-04583 standard, mine water from the Kleofas coal mine, and blast-furnace circulation water from the Częstochowa metallurgical plant were used in these studies.

Nitro derivatives of SE novolak were obtained by the nitration of linear-structure novolak with nitrating acid (HNO_3/H_2SO_4). The amino derivatives were obtained by the reduction of novolak nitro derivatives with a mixture of $SnCl_2/H_2O$ and concentrated HCl. The obtained products were separated and purified.[26]

The intrinsic viscosity was determined with an Ubbelohde viscometer with a Pollena K no. I capillary ($K = 0.02510$) at 298 ± 0.01 K. The measurements were conducted in a Julabo Labortechnik GmbH thermostat (Seelbach, Germany). The bulk density was measured according to the PN-64/C-98054 standard. The identification of the polymer characteristic groups and nitro and amino groups was done with a Perkin Elmer Spectrum One IR spectrometer (Shelton, CT). The samples were prepared in the form of tablets with 1 mg of the investigated compound and 100 mg of KBr. Spectra were recorded in the 4000–400-cm^{-1} range. The studies of the flocculation process were conducted according to the PN-71/C-04583 standard. The studies of the flocculation process were started after the selection of optimum doses of the coagulant and flocculent. This procedure was adopted because in sewage treatment plants, the anionic polyelectrolytes are used mainly for aiding the coagulation process. They are rarely used independently, in contrast to cationic polyelectrolytes. Solutions of the obtained products (0.1% and 0.01%) and a 1% solution of a standard coagulant (aluminum sulfate) were used in the flocculation tests. Before this, at the beginning of each measurement, the turbidity of the investigated water was determined. Then, the optimal dose of the coagulant was chosen in the following way. The investigated water (300 cm^3) was poured into a beaker, and then the specified amount of the coagulant was added. All of this was mixed with a mechanical stirrer for 1 min at 300 rpm and for 15 min at 90 rpm. After 30 min of sedimentation, the turbidity of the tested water was determined again. For a known dose of the coagulant, an optimum dose of the flocculent was then determined from the turbidity of the tested water. For this determination to be made, into a second beaker, the same amount of water was poured, and the specified dose of the coagulant was added. All of this was mixed with a mechanical stirrer for 1 min at 300 rpm and for 15 min at 90 rpm. After 30 min of sedimentation, the turbidity of the tested water was determined again. The turbidity was measured with a Bioblock

TABLE I
Synthesis and Properties of Nitro Derivatives of NS Novolak

Sample	Reaction temperature (K)	Yield (%)	Contents of N_2 and nitro groups		Molecular rate of nitration ω/dt (mol/min)
			%	w^a	
1	323	69	4.59	0.40	0.003
2	293	80	5.30	0.48	0.004
3	313	76	4.31	0.38	0.003
4	303	80	4.06	0.35	0.003
5	308	78	4.19	0.36	0.003

[a] Molar content of nitro groups per constitutional unit of resin.

Scientific Turb 550 IR (Illkirch, France) according to the ISO 797/DIN 27027 standard and U.S. Environmental Protection Agency recommendations.

RESULTS AND DISCUSSION

NS novolak production wastes containing about 4% free phenol were selected for this study. A commercial product of this novolak contains 3% free phenol at most. For nitro derivatives of the wastes under study, the percentage content of nitrogen (Table I) and the melting temperature were determined. For the amino derivatives, the bulk density and intrinsic viscosity were also found. The obtained derivatives were tested as potential flocculants (Table II).

The nitration of the NS novolak production wastes was conducted at 293–323 K for 2 h with a molar ratio of novolak to nitration acid (HNO_3 + H_2SO_4) of 1:1.5: 2.5 with a 50% excess of HNO_3. The products contained 4.06–5.30% nitrogen (Table I) and had the form of light orange or dark brown powders. In the process of NS novolak nitration, the maximum concentration of nitro groups was achieved in 2 h at 293 K.

The yield of the nitration process was 69–80%. The reaction yield decreased with an increase in the temperature. The melting points of the NS novolak nitro derivatives were 459–476 K. The NS novolak waste nitration products were insoluble in nitrobenzene, cyclohexane, acetic acid, dimethylformamide (DMF), xylene, ethyl acetate, toluene, pyridine, benzene, nitrobenzene, aniline, dioxane, and water. However, the nitro derivatives of the NS novolak production waste were very soluble in dilute (3%) solutions of KOH and NaOH.

The nitration products of the NS novolak production waste were then reduced into amino derivatives to obtain synthetic anionic-type polyelectrolytes. The amino derivatives contained 0.75–2.95% nitrogen, which corresponded to one amino group per three to eight constitutional units (Table II).

The bulk density of the amino derivatives of the NS novolak production waste was 0.589–0.757 g/cm^3. This corresponded to the bulk density of the commercial polyelectrolyte and was half that of the initial novolak. The intrinsic viscosities of the amino derivatives of the NS novolak production waste were 0.19–0.29 dm^3/g. These values corresponded to the intrinsic viscosities of a standard polyacrylamide (molecular weight = 5.09 $\times$ 10^5) synthesized by the precipitating method. The melting temperatures of the products were greater than 490 K and greater than the melting temperature of the nitro derivatives of NS novolak.

The solubility of the synthesized amino derivatives of the SE novolak production waste in a given organic solvent and water was examined at both room temperature and the boiling temperature of the solvent. These products were insoluble in butanol, acetic acid, isopropanol, DMF, xylene, cyclohexanol, ethyl acetate, pyridine, toluene, benzene, nitrobenzene, cyclohexane, aniline, dioxane, and water. Because the NS novolak amino derivatives were insoluble in water, their solubility in dilute (3%) solutions of KOH or NaOH was

TABLE II
Properties of Amino Derivatives of NS Novolak Obtained in the Reduction Process of Nitro Derivatives

Sample	Yield (%)	Contents of N_2 and amino groups		Number of constitutional units per NH_2 group	Bulk density (g/cm^3)	Intrinsic viscosity (dm^3/g)
		%	w*			
1	94	0.75	0.05	8	0.757	0.13
2	89	0.99	0.08	7	0.677	0.15
3	99	1.23	0.10	7	0.589	0.17
4	94	1.50	0.11	7	0.703	0.19
5	87	2.95	0.23	3	0.702	0.28

[a] Molar content of amino derivatives of NS novolak obtained in the reduction process of nitro derivatives.

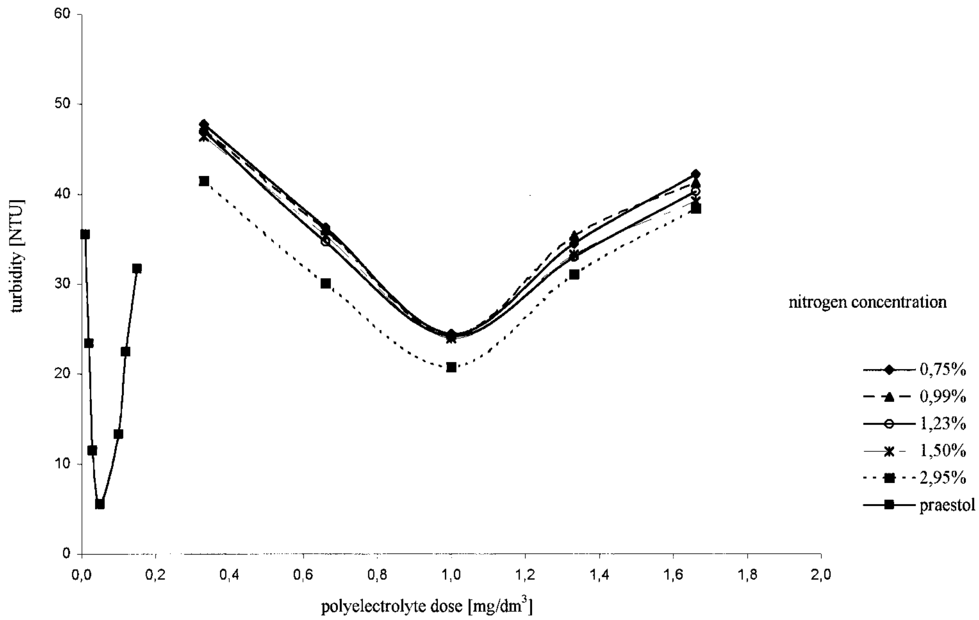

Figure 1 Dependence of the turbidity on the polyelectrolyte dose [an amino derivative of NS novolak (phenol-formaldehyde resins) and Praestol 2515] for various concentrations of amino groups in the polymer during the treatment of water from the Kleofas coal mine with an initial turbidity of 177 NTU (the turbidity after coagulation was 39.6 NTU at a coagulant dose of 66.7 mg/dm^3 and pH 6.96).

also examined; they were very soluble in these solutions. Therefore, the solutions of these derivatives in dilute water solutions of KOH were used to test their applications as polyelectrolytes in flocculation processes.

A comparative analysis of IR spectra showed that bands at 1541 and 1344 cm^{-1}, characteristic of nitro derivatives, did not appear on spectra of the amino derivatives of NS novolak. A broad absorption band at 3444 cm^{-1} on the spectra of the amino derivatives of NS novolak confirmed the existence of NH_2 groups. This band corresponded to the asymmetric valence vibration of NH_2 groups.

The amino derivatives of the NS novolak production waste were also tested as flocculants for sewage and model water treatment. The results of the application of the obtained amino derivatives of the NS novolak production waste in the flocculation process of sewage treatment are given in Figures 1 and 2.

First, the optimum dose of the coagulant was determined. For water from the Kleofas coal mine, this was found to be 66.7 mg of aluminum sulfate/dm^3 of water, whereas for water from the Częstochowa metallurgical plant power plant circulation system, this dose was 100 mg. For comparison, similar studies of the flocculation process were also conducted with a weak alkaline commercial polyelectrolyte (Praestol 2515) obtained from polyacrylamide (Figs. 1 and 2).

It was found from the study of the flocculation process that the coagulation-aiding effect of the NS novolak amino derivatives was two times lower than that for Praestol 2515, even for a three times greater concentration of these derivatives. This was probably due to the lower molecular weight of the obtained NS novolak amino derivatives (Figs. 1 and 2). The highest decrease in turbidity was obtained for Praestol 2515. The following values were obtained: 31.9 NTU at 0.05 mg/dm^3 for water from the Kleofas coal mine, that is, 86.1% of the turbidity value obtained before flocculation, and 70.1 NTU at 0.1 mg/dm^3 for power plant circulation water from the Częstochowa metallurgical plant, that is, 59.1% of the turbidity value obtained before flocculation. The best results for the flocculation aiding process were obtained for the amino derivatives of novolak with the highest percentages of nitrogen (1.50 and 2.95%, respectively) and highest intrinsic viscosities (0.19 and 0.28 dm^3/g, respectively). The minimal turbidity values after the flocculation process with the use of amino derivatives of the NS novolak waste as polyelectrolytes at a concentration of 1.000 mg/dm^3 were as follows: 20.8 NTU for water from the Kleofas coal mine (decrease in turbidity = 18.8 NTU), that is, 47.5% of the turbidity value before flocculation, and 71.4 NTU for blast-furnace circulation water from the Częstochowa metallurgical plant (decrease in turbidity = 47.2 NTU), that is, 39.8% of the turbidity value before flocculation.

For the Praestol 2515 polyelectrolyte, the decrease in the turbidity of the investigated waters was significantly higher at lower polyelectrolyte concentrations and in a narrow range of concentrations, whereas the SE novolak amino derivatives were effective at higher concentrations and over a significantly wider concentration range. Moreover, an increase of the amino groups in the polymer per constitutional unit in modified NS novolak production wastes led to a turbidity

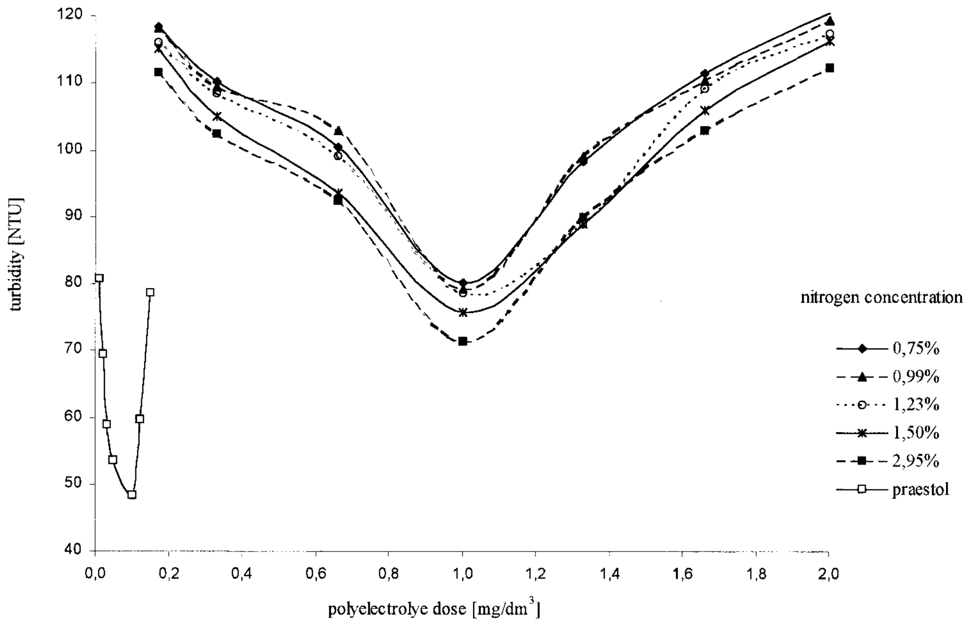

Figure 2 Dependence of the turbidity on the polyelectrolyte dose [an amino derivative of NS novolak (phenol-formaldehyde resins) and Praestol 2515] for various concentrations of amino groups in the polymer during the treatment of water from the Częstochowa metallurgical plant circulation system with an initial turbidity of 247 NTU (the turbidity after coagulation was 118.6 NTU at a coagulant dose of 100 mg/dm^3 and pH 6.94).

decrease in the analyzed water for the same concentration of polyelectrolytes. The lack of a correlation between the viscosity of the amino derivatives and the polyelectrolyte concentration causing a maximum turbidity decrease in the analyzed water was observed. This suggested that the change in the intrinsic viscosity of the modified polymer wastes depended not on the molecular weight but on the amino group concentration in the modified polymer.

The observed constant polyelectrolyte concentration for a maximum decrease in the analyzed water turbidity at various polyelectrolyte viscosities proved indirectly that during nitration and nitro group reduction processes, the destruction processes of phenol-formaldehyde resins were not observable or were negligible.

The results of flocculation process studies of water from the Kleofas coal mine showed that the obtained amino derivatives of the NS novolak production waste could be used with good effect as anionic-type flocculants for water exhibiting a high turbidity of 177 NTU (total amount of suspension $\sim$ 60 mg/dm^3) and containing significant amounts of sulfates and chlorides (sulfates $\sim$ 1500 mg of SO_4/dm^3 and chlorides $\sim$ 1700 mg of Cl/dm^3). They could also be used as flocculants of water from the Huta Częstochowa plant circulation system, which exhibited a turbidity of 247 NTU (total amount of suspension $\sim$ 14 mg/dm^3) and contained sulfates ($\sim$140 mg/dm^3) and chlorides ($\sim$1400 mg/dm^3; Table III and Figs. 1 and 2).

For the selected sewage used for the flocculation studies with the application of the novolak NS waste amino derivatives, a full analysis of the impurities was conducted. The analysis was performed for water before and after purification with the obtained polyelectrolytes according to a standard (Table III). Although the initial compositions of the sewage from the Kleofas coal mine and the Huta Częstochowa plant circulation system were significantly different, the amounts of the flocculent necessary for a maximum decrease in turbidity were similar. At first glance, it seemed that the flocculation mechanism was different in both cases. This phenomenon might be connected to the fact that, in this procedure, the charge neutralization mechanism dominates. This hypothesis needs further detailed studies. Additionally, the concentrations of all the impurities significantly decreased in the investigated water after the treatment process. A more significant drop in the concentration was observed for the solvated part, the sulfates and chlorides. A drop in five-day biochemical oxygen demand (BZT), oxygen consumption: dichromate method (ChZT), and oxygen demand was also observed. The analyzed sewage after the treatment process using the amino derivatives of the NS novolak production wastes were accepted (according to standards) for disposal into water.[27]

CONCLUSIONS

Phenol-formaldehyde resin (NS novolak) wastes could be used for obtaining effective anionic-type polyelectrolytes. This could be a solution for their recycling. The amino derivatives of the novolak NS production wastes exhibited good flocculation properties, but they were worse than those of the commer-

TABLE III
Analysis of Waters from Kleofas Coal Mine and from Huta Częstochowa Power Plant Circulation System After the Coagulation and Flocculation Process with the Synthesized Polyelectrolytes (Amino Derivatives of Phenol-Formaldehyde Resin Production Wastes: NS novolak)

Determined water property	Analysis value of the treatment from, Kleofas coal mine		Analysis value of the water from the power plant circulation system of Huta Częstochowa	
	Before purification	After purification	Before purification	After purification
Reaction (pH)	6.69	7.21	6.94	7.45
Solvated oxygen (mg of O_2/dm^3)	7.7	8.1	—	—
Phenols (mg/dm^3)	—	—	5.1	<0.005
Cyanides (mg/dm^3)	—	—	1.8	<0.005
Five-day biochemical oxygen demand (mg/dm^3)	4.9	1.9	—	—
Oxygen consumption: dichromate method (mg of O_2/dm^3)	15.8	120.0	185.4	125.0
Detergents (mg/dm^3)	<0.1	<0.1	—	—
Ether extract (mg/dm^3)	5.0	2.0	12.9	8.0
Ammonia nitrogen (mg/dm^3)	0.18	0.5	284.0	0.41
Sulfates (mg of SO_4/dm^3)	1510.0	51.4	141.8	95.5
Chlorides (mg of Cl/dm^3)	1710.0	13.5	1386.0	42.3
Manganese (mg of Mn/dm^3)	0.85	<0.15	—	—
Total iron (mg of Fe/dm^3)	0.45	<0.50	—	—
Total hardness ($mval/dm^3$)	50.7	2.4	13.67	2.3
Solvated parts: total amount (mg/dm^3)	5120.0	280.0	4465.0	394.0
Suspension: total amount (mg/dm^3)	78.0	12.8	13.2	10.8

Experiments were conducted in the given industrial plants.

cial polyelectrolyte Praestol 2515 and at much higher concentrations. They could be used as polyelectrolytes, aiding flocculation and improving the sedimentation conditions of water with properties like those of water from the Kleofas coal mine and the Huta Częstochowa power plant circulation system.

The synthesis of phenol-formaldehyde resins from waste phenol and their modification into sulfo or amino derivatives[4–8] could constitute a new tool for phenol waste management. For diminishing the phenol hazard to the environment, this type of resin is being produced and stored for further use. Chemically bound phenol is not a hazard to the environment, and it is relatively easy to obtain permission for its storage.

References

1. Metz, G. Kunststoffe 1995, 85, 1504.
2. Yasuhito, I.; Miyuki, K.; Tsutomu, N.; Haruo, W. Am Chem Soc 1999, 15, 4171.
3. Simitzis, J.; Fountas, D. J Appl Polym Sci 1995, 55, 879.
4. Bajdur, W.; Sułkowski, W. Inżynieria Ochrona Środowiska (in Polish) 1998, 1, 115.
5. Bajdur, W.; Sułkowski, W. Chem Inżynieria Ekologiczna (in Polish) 2000, 7, 119.
6. Bajdur, W.; Sułkowski, W. Chem Inżynieria Ekologiczna (in Polish) 2000, 7, 129.
7. Bajdur, W.; Pajączkowska, J.; Makarucha, B.; Sułkowska, A.; Sułkowski, W. W. Eur Polym J 2002, 38, 299.
8. Bajdur, W.; Sułkowski, W. Polym Recycl 2001, 6, 71.
9. Wastewater Engineering: Treatment, Disposal and Reuse; Tchobanoglous, G.; Burton, F. L., Eds.; McGraw-Hill: New York, 1991.
10. Gregory, J. Chemistry and Technology of Water-Soluble Polymers; Plenum: New York, 1983.
11. Rosse, G. R.; St. John, M. R. Encyclopedia of Polymer Science and Engineering, 2nd ed.; Wiley: New York, 1986; Vol. 7.
12. McCormick, C. L.; Bock, J.; Schulz, D. N. Encyclopedia of Polymer Science and Engineering, 2nd ed.; Wiley: New York, 1986; Vol. 17.
13. Gregory, J. Colloids Surf 1988, 31, 231.
14. Tanaka, M.; Swerin, A.; Odberg, L. Tappi J 1993, 76, 157.
15. Lafuma, F. Polimery TW 1998, 43, 104.
16. Mabire, F.; Audebert, R.; Quivaron, C. J Colloid Interface Sci 1984, 97, 120.
17. Hocking, M. B.; Klimchuk, K. A.; Lowen, S. J Macromol Sci Rev Macromol Chem Phys 1999, 39, 177.
18. Wong, K.; Lixon, P.; Lafuma, F.; Lindner, P.; Aguerre Charriol, O.; Cabane, B. J Colloid Interface Sci 1992, 153, 55.
19. Lafuma, F.; Wong, K.; Cabane, B. J Colloid Interface Sci 1991, 143, 9.
20. Mabire, F.; Audebert, R.; Quivaron, C. J Colloid Interface Sci 1984, 97, 120.
21. Coagulation and Flocculation; Dobias, B., Ed.; Marcel Dekker: New York, 1993.
22. Leong, Y. K. Colloid Polym Sci 1999, 277, 299.
23. Nowicki, W.; Nowicka, G. Wiadomości Chem (in Polish) 2001, 55, 547.
24. Petzold, G.; Buchhammer, H.; Lunkwitz, K. Colloids Surf 1996, 119, 87.
25. Harland, R. S.; Prud'homme, R. K. Polyelectrolytes Gels—Properties, Preparation and Application; American Chemical Society: Washington, DC, 1992.
26. March, J. Advanced Organic Chemistry: Reactions, Mechanisms and Structure; Wiley: New York, 1992.
27. Supplement to the Decree of the Ministry of Environmental Protection, Natural Resources and Forestry (Dziennik Ustaw Nr 116, Warszawa, Poland). In Data of Environmental Pollutant Concentration in Water (in Polish); 1991.