Electronic Structure and Ground State Properties of PMMA Polymer: II. Protection of PMMA Against Gamma Irradiation Damage

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The equilibrium ground state geometric parameters of N,N,N′,N′,-tetraoxaloylsulphanilamide (Ligand I), N,N-dioxaloylbenzenesulpony-N′,N′,-dioxaloylthiocarbazide (Ligand II) and p-N,N-dioxaloylaminobenzene-N′,N′-dioxaloylbenzenesulphonyloxamide (Ligand III) as polyfunctional ligands were investigated theoretically using AM1-MO method. The expected biradicals formed after gamma radiolysis for each ligand can be detected. The radiation protection of the PMMA matrix from gamma rays, using the biradicals formed of ligands (I), (II), and (III), can be considered theoretically. The structure of the protected chains formed after recombination of two symmetric chains with biradical are theoretically modelled, because in the reaction medium the chain of PMMA formed is asymmetric. All interpretations concerning the ground state properties of the protected chains are qualitative. The thionyl, phenyl, and benzenesulphonyl biradicals are more efficient than carbonyl, thioamides, and sulphonyl biradicals as indicated from the MO-results, molecular weight investigation, and infrared spectroscopy. The protection of PMMA by the formed biradicals is confrmed by proton NMR spectroscopy.

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INTRODUCTION

Chemical groups differ widely in their sensitivity to radiation. This may be seen, for example, in the different G-values for radical production in simple organic compounds and in the wide range of G-values for crosslinking and degrading polymers [1]. The sensitivity of a chemical group to radiation is, however, a purely relative term and it may be greatly modified by the presence of other groups either in the same or in adjacent molecules. When the effect is to reduce the reactivity of a major component of the system by the presence of another component or additive, one refers to radiation protection. This is a generic term indicating the effect observed experimentally, and may arise through a number of possible mechanisms such as energy transfer, radical-radical reactions, or repair processes [2].

Generally, there are two types of radiation protection. The first is the internal radiation protection, which could occur due to resonance effects in low molecular weight compounds such as aromatic derivatives [3]. The second type of radiation protection is the external protection [4]. The sensitivity of a polymer to radiation may be suppressed by the use of additives [5–9]. Such additives are often referred to as protectors. The concentration of these additives may be quite low, of the order of a few percent. Although radiation protection has been found to occur in irradiated polymers in the solid or liquid state and in solution [10], the amount of quantitative data available in this field is as yet very scant. In the absence of any systematic study of the electronic properties and bonding characteristics of the protection process of PMMA polymers, most conclusions that relate the recombination process to structural factors are qualitative. The main objective of the present article is to:

1. Synthesize new polyfunctional organic ligands, namely N,N, N′,N′-tetraoxaloylsulphanilamide (ligand I),N,N,-dioxaloylbenzene-sulponyl-N′,N′-dioxaloylthiocarbazide (ligand II) and p-N′,N′-dioxaloylamino benzene-N′,-N′-dioxaloylbenzenesulphonyloxamide (ligand III).
2. Explore the effects of geometric features of the prepared ligands upon gamma radiolysis and investigate the expected biradicals formed.
3. Investigate closely the ground state electronic structure parameters and the stability of the recombined biradical-polymer radical molecule.

EXPERIMENTAL

Preparation of the Organic Ligands

N,N,N′,N′-Tetraoxaloylsulphanilamide

This new organic chelating agent was prepared by condensation of sulphanilamide (0.1 mole) and oxalic acid (0.4 mole) in a xylene medium, using Dean and Stark apparatus. The theoretical amount of water was removed to produce N,N,N′,N′-tetraoxaloylsulphanila-mide, which has a melting point of 210°C. After crystallization from distilled water the yield was found to be 82.5%.

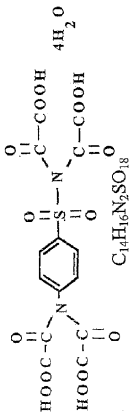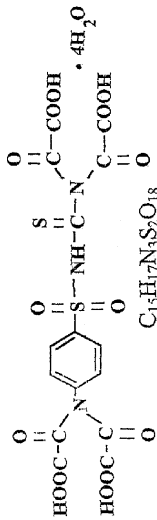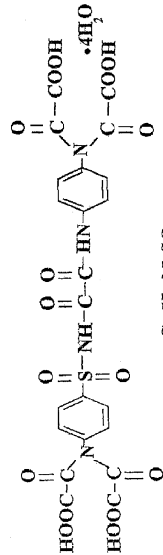### *N′, N′-Dioxaloylbenzenesulponyl-N′, N′-dioxaloyl thiocarbazide*

This new organic chelating agent was prepared by mixing sulphanil-amide (0.1 mole) in glacial acetic acid water mixture (2:5 V/V) as a medium. The flask content was warmed for five minutes, and then ammonium isothiocyanate (0.1 mole) was added, the flask content was refluxed for one hour and left to cool, then filtered and recrystalized from 50% acetic acid/water mixture (V/V). The N-thioureadisulphanilamide (0.1 mole) is condensed with oxalic acid (0.4 mole) in a xylene medium, using Dean and Stark apparatus. The theoretical amount of water was removed to produce N,N-dioxaloylbenzenesulponyl-N′,N′-dioxa-loylthiocarbazide, which has a melting point of 180°C. After crystalliza-tion from distilled water the yield was found to be 84.5%.

p-N,N-Dioxaloylaminobenzene-N′, N′-dioxaloylbenzenesulphonyl oxamide

This new organic chelating agent was prepared by condensation of p-phenylenediamine with oxalic acid (0.1 mole) in a xylene medium, using Dean and Stark apparatus. The theoretical amount of water was removed to produce N-oxaloyl-p-phenylenediamine. The N-oxaloyl-p-phenylenediamine was condensed with sulphanilamide in a xylene medium, using Dean and Stark apparatus. After removing the theo-retical amount of water, oxalic acid (0.4 mole) was added to the reaction medium. Then, the theoretical amount of water was removed to produce p-N,N-dioxaloylaminobenzene-N′,N′-dioxaloylbenzenesulpho-nyloxamide, which has a melting point of 220°C. After crystallization from distilled water the yield was found to be 79.5%.

All the prepared organic ligands were recrystallized from distilled water and dried in an oven at 70°C till constant weight. The elemental analysis of these substances is summarized in Table 1.

TABLE 1 Analytical Data of the Prepared Ligands

| No.	Molecular formula	Elemental analysis (Calc/Found)				Mol.Wt. Calc/ Found	Acid value Calc/ Found	pK_1– pK_4 Value
		C%	H%	N%	S%			
(I)	$C_{14}H_{16}N_2SO_{18}$	31.67 32.40	3.01 3.50	5.26 6.0	6.01 6.8	532 539	421.8 430.5	1.86 2.13 6.92 9.70
(II)	$C_{15}H_{17}N_3S_2O_{18}$	30.45 31.40	2.87 3.10	7.10 6.8	10.8 10.2	591 595	379 371	1.65 1.89 5.71 9.75
(III)	$C_{22}H_{22}N_4SO_{20}$	38.90 39.50	3.17 4.10	8.10 8.3	4.6 5.0	694 698	323 320	1.95 2.75 6.75 10.3

Molecular Orbital Calculations

All molecular orbital calculations were carried out using the reliable semi-empirical AM1-MO method [11], because it takes very good account of the directional character of bonding and describes a polar bond more accurately than any other methods.

RESULT AND DISCUSSION

Ligand Structure

Numbering system and final geometry of N,N,N′,N′-tetraoxaloyl sulphanilamide (Ligand I), N,N-dioxaloylbenzenesulponyl-N′,N′-dioxaloyl thiocarbazide (Ligand II) and p-N,N-dioxaloylaminobenzene-N′,N′-dioxaloyl benzenesulphonyloxamide (Ligand III) are represented in Figure 1. Net charge and π-bond order of the ligands (I), (II), and (III) are represented in Table 2. Some general remarks on the obtained data are summarized as follow:

1. The active centers of ligand (I) are S7, O8, O9, N10, N21 and phenyl moiety, as indicated from the net charge located on each atom. All centers are π-acceptors and σ-donors except sulphur atom, which is σ-acceptor (c.f. Table 2).
2. The estimated π–bond order of pairing atoms in ligand I (C3-N21, C6-S7, S7-N10, C11-N10, and C16-N10) are very small. Therefore, these types of bonds are purely single bond, which can be broken under the effect of gamma rays.
3. The expected biradicals, which could be formed after gamma radiolysis of ligand (I), are given in Table 3.
4. The active centers of ligand (II) are S7, O8, O9, S12, N10, N13, N24, and phenyl moiety. All centers are strong π-acceptor except S7 and S12 atoms, which are σ-acceptor (c.f. Table 2).
5. The estimated π-bond order of pairing atoms in ligand II (C3-N24, C6-S7, S7-N10, N10-C11, and C11-N13) are very small, of the order of ($\approx$0.1), indicating the absence of conjugation between different moieties of ligand (II), which is the reason for biradical formation upon gamma radiolysis.
6. The expected biradicals formed after gamma radiolysis of ligand (II), are summarized in Table 3.
7. The active centers of ligand (III) are O9, N11, O8, S7, N10, C28, O29, C30, O31, N32, N39, Ph-N, and Ph-S moieties.
8. The estimated π-bond order of pairing atoms in ligand III (N11-C3, C6-S7, S7-N10, C28-C30, N32-C33, and C36-N39) are very small ($\approx$0.05) indicating no conjugation between these moieties. On the
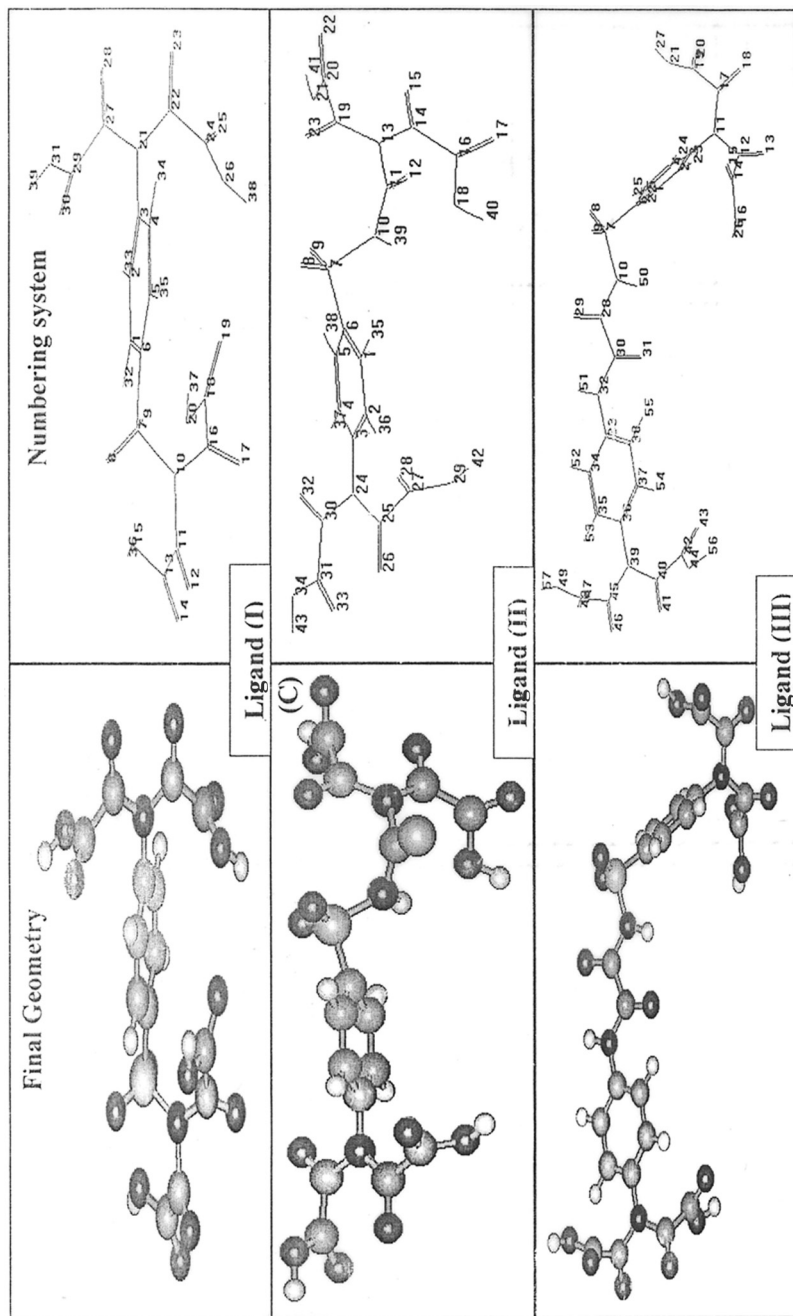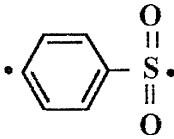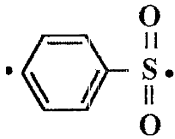
FIGURE 1 Final geometry and numbering system of the prepared ligands.

TABLE 2 The π-Bond Order and Net Charge for the Prepared Three Ligands

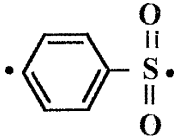| Ligand (I)				Ligand (II)				Ligand (III)			
Bond	P-π	Atom	Net charge	Bond	P-π	Atom	Net charge	Bond	P-π	Atom	Net charge
C6-S7	0.044	S7	2.8606	C3-N24	0.057	S7	2.8438	C3-N11	0.057	S7	2.8588
S7-O8	0.413	O8	-0.8823	C6-S7	0.041	O8	-0.9058	C6-S7	0.038	O8	-0.9014
S7-O9	0.401	O9	-0.8999	S7-O8	0.393	O9	-0.8997	S7-O8	0.405	O9	-0.9071
S7-N10	0.044	N10	-0.8154	S7-O9	0.388	N10	-0.8544	S7-O9	0.398	N10	-0.8317
N10-C11	0.106	N21	-0.3014	S7-N10	0.063	S12	0.1985	S7-N10	0.052	N11	-0.3248
N10-C16	0.110	Ph-	-0.3774	N10-C11	0.109	N13	-0.3460	N10-C28	0.206	C28	0.3120
N21-C3	0.064			C11-N13	0.046	N24	0.2945	N11-C12	0.116	O29	-0.3083
				N13-C19	0.153	Ph-	-0.3617	N11-C17	0.181	C30	0.2969
				N13-C14	0.186			C28-C30	0.025	O31	-0.3343
								C30-N32	0.275	N32	-0.2949
								N32-C33	0.097	N39	-0.3087
								C36-N39	0.081	Ph-S	+0.2165
								N39-C45	0.097	Ph-N	-0.1161
								N39-C40	0.162		

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TABLE 3 The Biradicals that Can Be Formed in the Prepared Ligands During Gamma Radiolysis

Ligand (I)	Ligand (II)	Ligand (III)

other hand, the bond order of N10-C28 and C30-N32 are 0.2 and 0.3 respectively, that is, a considerable partial π-bond character of these bonds. Therefore, the presence of -NH-CO- biradical becomes improbable at low temperature, which is confirmed by ^{1}H-NMR analysis: (c.f. Figure 2).

9. The expected biradicals formed upon gamma radiolysis of ligand (III) are given in Table 3.
10. Table 3 presents the similarities and the differences of the biradicals formed upon gamma radiolysis in the three prepared ligands.
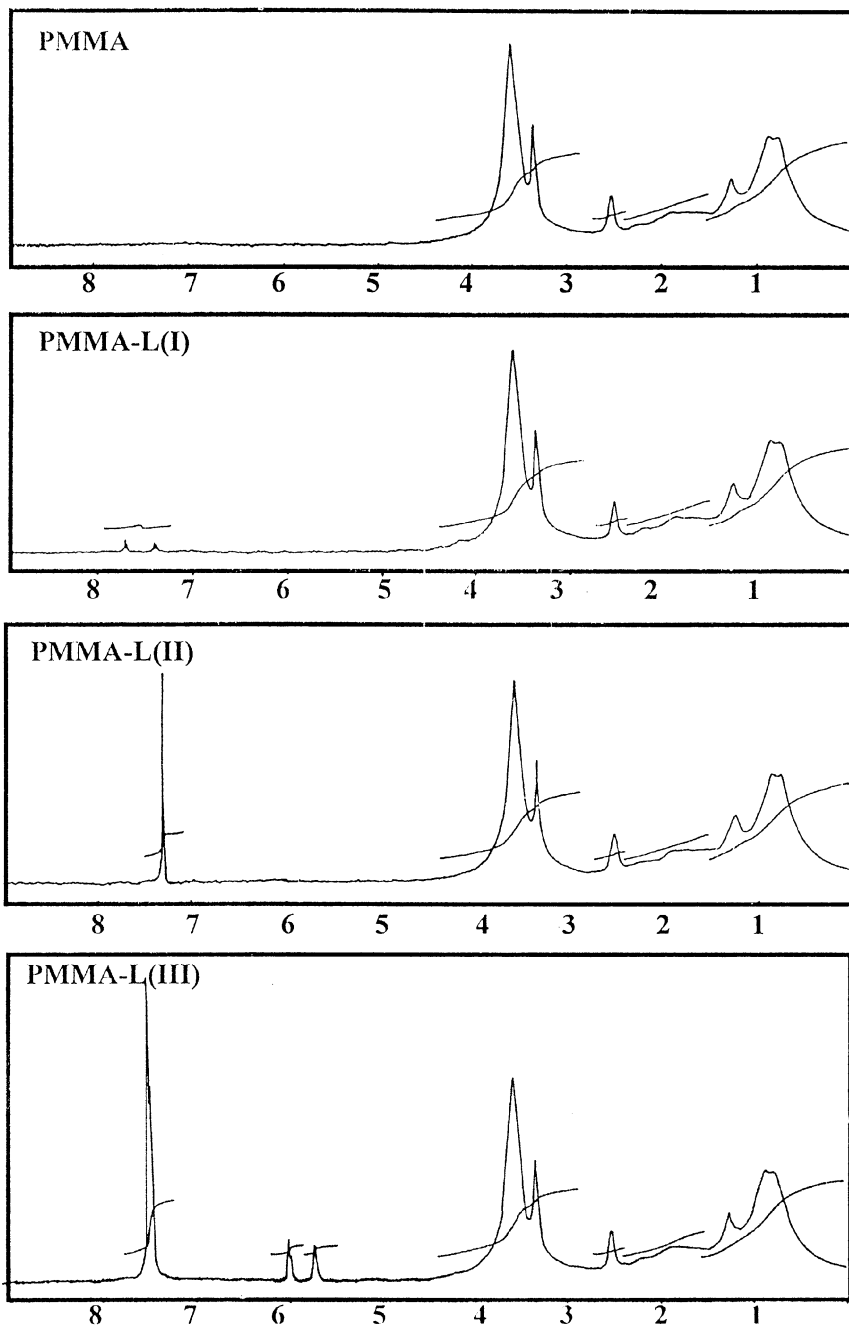
FIGURE 2 ^{1}H-NMR spectra of PMMA after irradiation with 50 kGy and extraction of the additives by solvent extraction and filtration.

## Protection of PMMA against Gamma Irradiation Damage

Radiation protection mechanism by using the biradicals formed from the cleavage of the prepared ligands upon gamma radiolysis may be considered to operate through the following two alternatives. (i) Some energy transfer may take place from PMMA to the additive, where the polymer being chemically unaltered, and (ii) the additive may repair the damage caused by gamma radiation. The additive itself may not suffer as a consequence. In PMMA polymers, the major reaction is a loss of hydrogen atom leaving a polymer radical $P^{\cdot}$. Protection against further reactions can occur if the additive itself furnishes a hydrogen atom and remains as a radical with new activity.

The final geometry and charge density maps of each two polymeric radicals with the biradical groups (c.f. Table 3) are presented in Figures 3–9. The ground state properties of the protected chains are given in Table 4. In this discussion the authors consider only the syndiotactic radical of PMMA as a stable structure [12], the total energy, E_T, which measures the stability of the chain, the dipole moment, μ, which measures the polarization, heat of formation, ΔH_f, which measures to some extent thermodynamically the formation of the protected chains and energy gap, and $\Delta\epsilon$, which measures the competitive interaction between different moieties. Some general remarks can be considered concerning the obtained data:

1. The recombination process depends on the biradical formed in the reaction medium during the gamma radiolysis. The biradical $(\dot{A})$ when existing in sufficient amount becomes the most efficient in the recombination process.

2. The structure of the protected chain formed after recombination of the two polymeric radicals and the biradical produced from the organic ligand (c.f. Figures 3–9) are theoretically modelled because the chains used are symmetric that is, the two polymeric radicals around $(\dot{A})$ biradical are the same. In the polymer matrix of PMMA, the formed radicals during gamma radiolysis are asymmetric. Therefore, all interpretation concerning the chains protection are qualitative.

3. The protected chains cannot be arranged in an order to describe the efficiency of chain protection during gamma radiolysis, because the size of the biradical $(\dot{A})$ is not equal (e.g., phenyl biradical and sulphonyl biradical). On the other hand, the molecular weight of biradical moiety is very small with respect to the molecular weight of the polymeric chain. Therefore, the total energy can be used to compare the different protective chains.
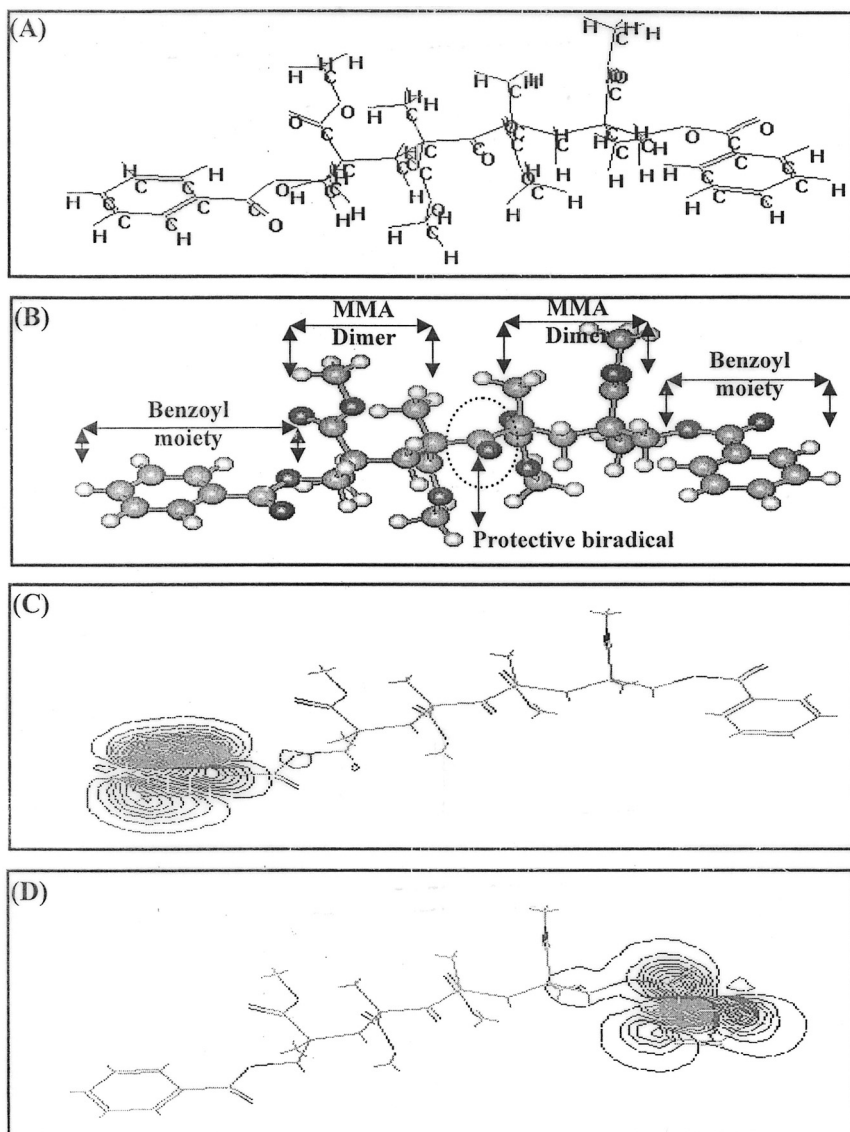
FIGURE 3 Final geometry (A) and (B), (C) HOMO, and (D) LUMO of PMMA protected by carbonyl biradical.
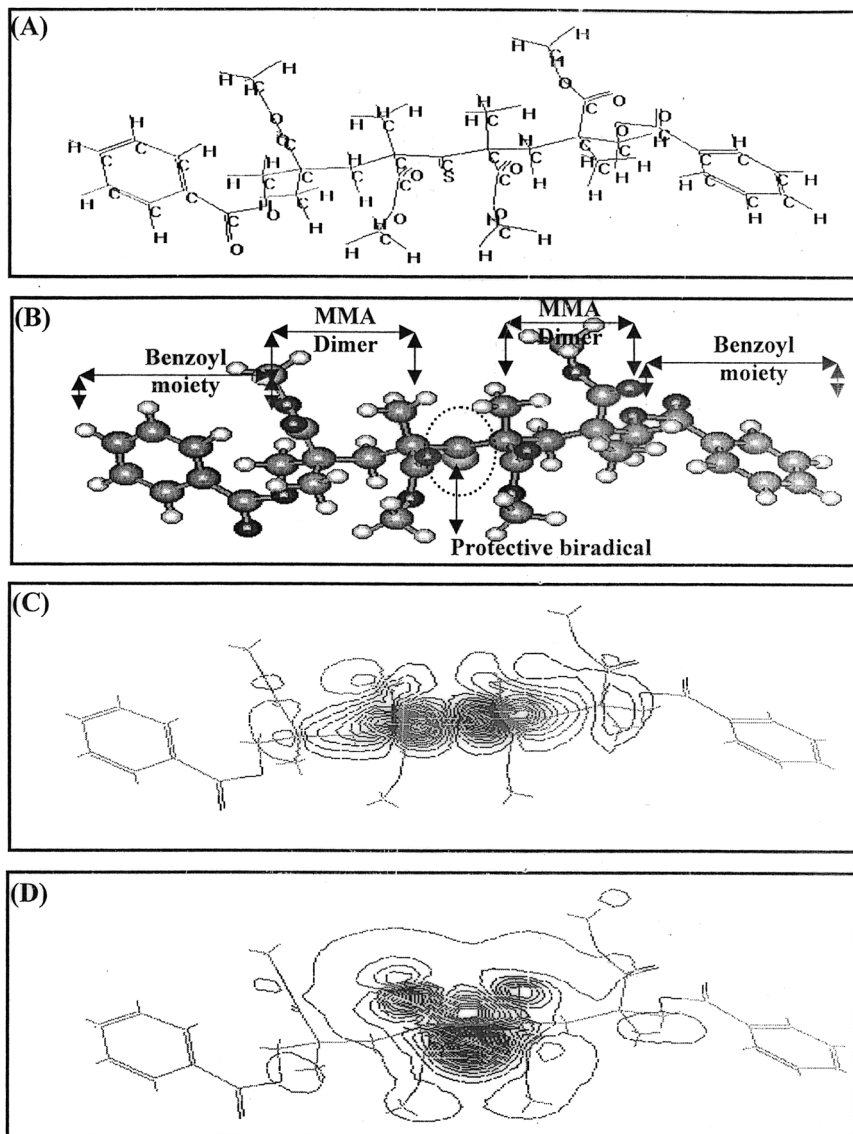
FIGURE 4 Final geometry (A) and (B), (C) HOMO, and (D) LUMO of PMMA protected by thiocarbonyl biradical.
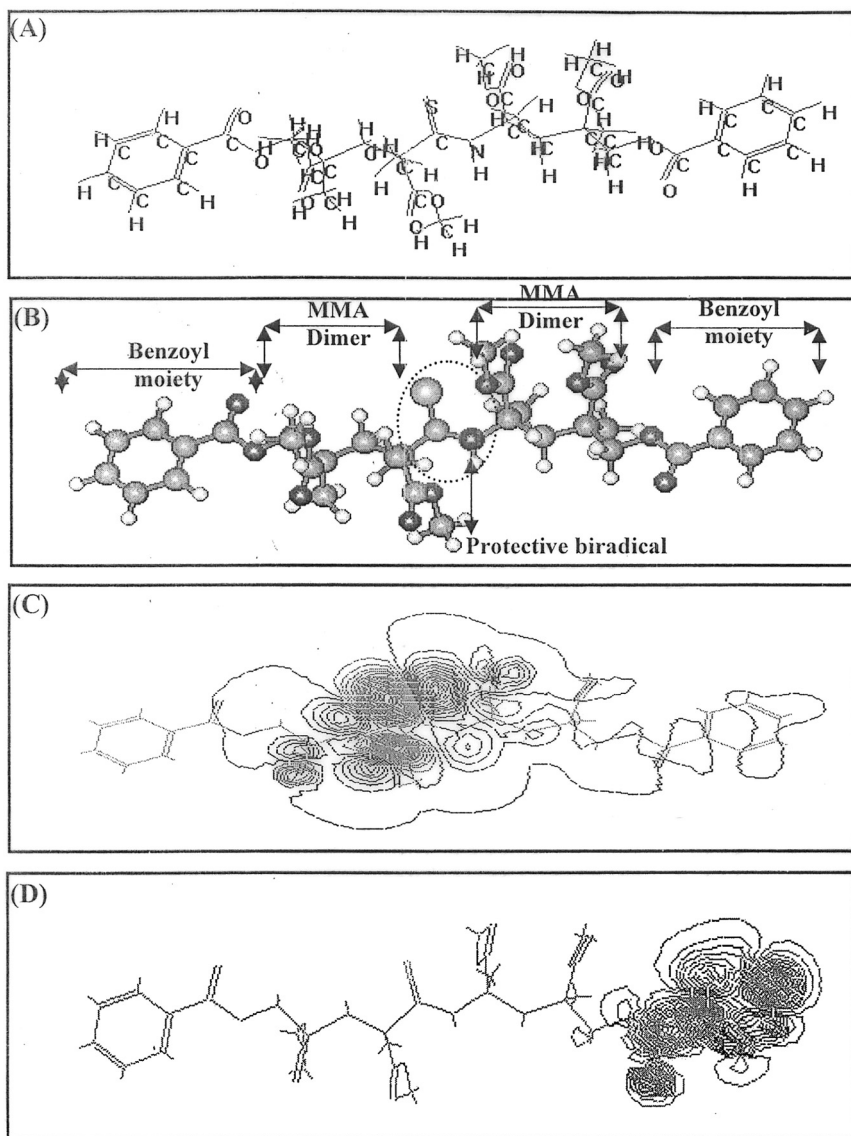
FIGURE 5 Final geometry (A) and (B), (C) Total, (D) HOMO, and (E) LUMO of PMMA protected by thioamide biradical.

FIGURE 6 Final geometry (A) and (B), (C) Total, (D) HOMO, and (E) LUMO of PMMA protected by biamide biradical.
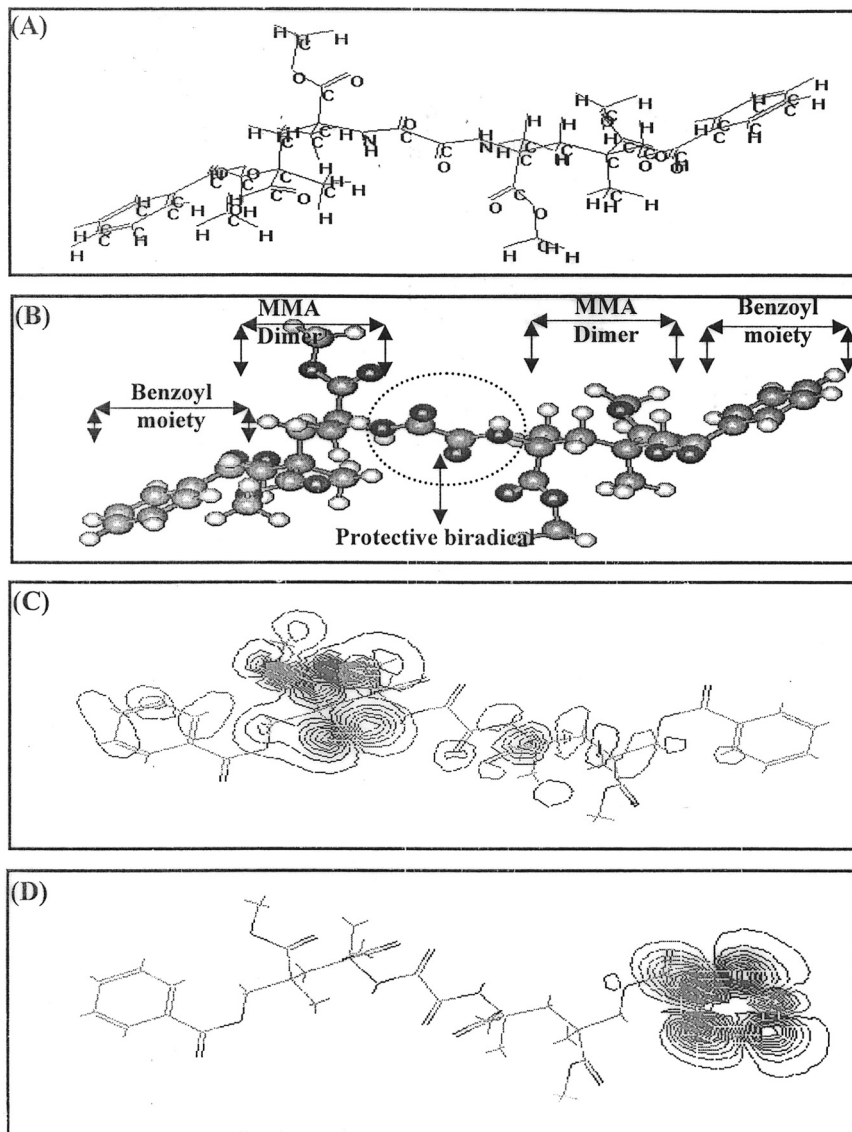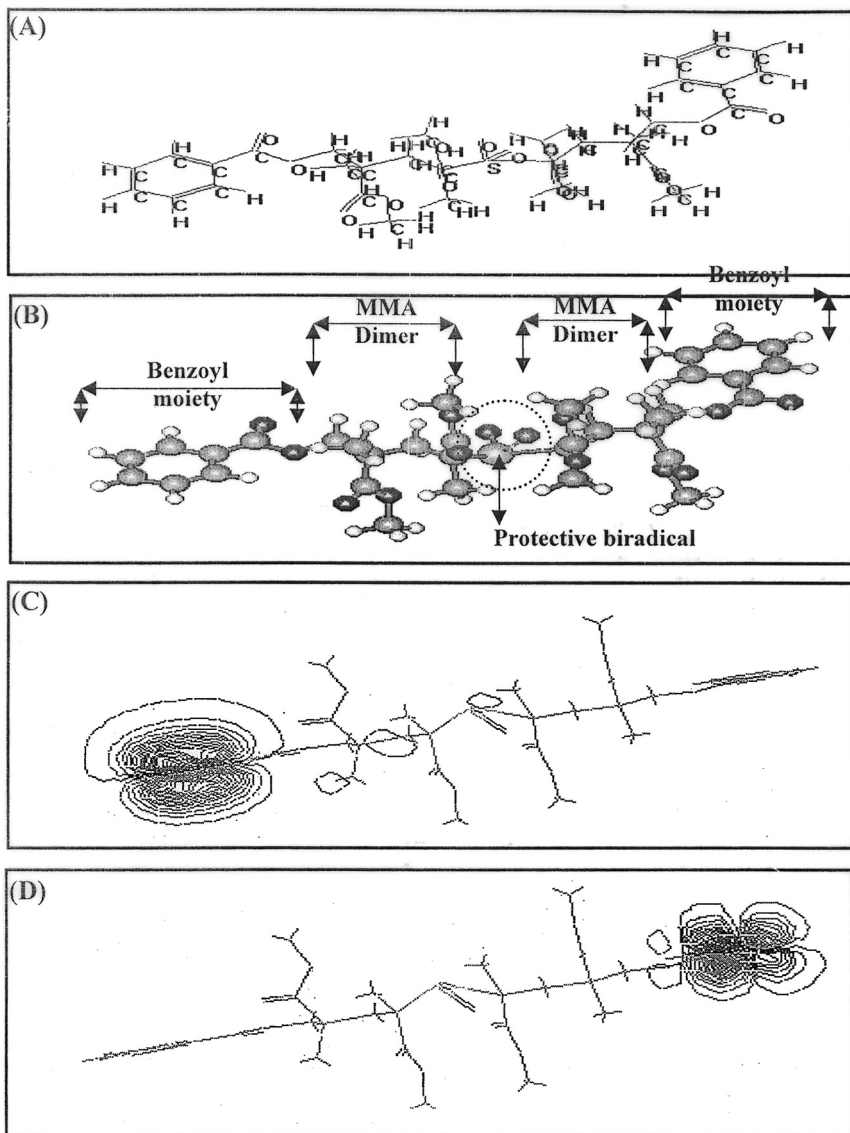
FIGURE 7 Final geometry (A) and (B), (C) HOMO, and (D) LUMO of PMMA protected by sulphonyl biradical.
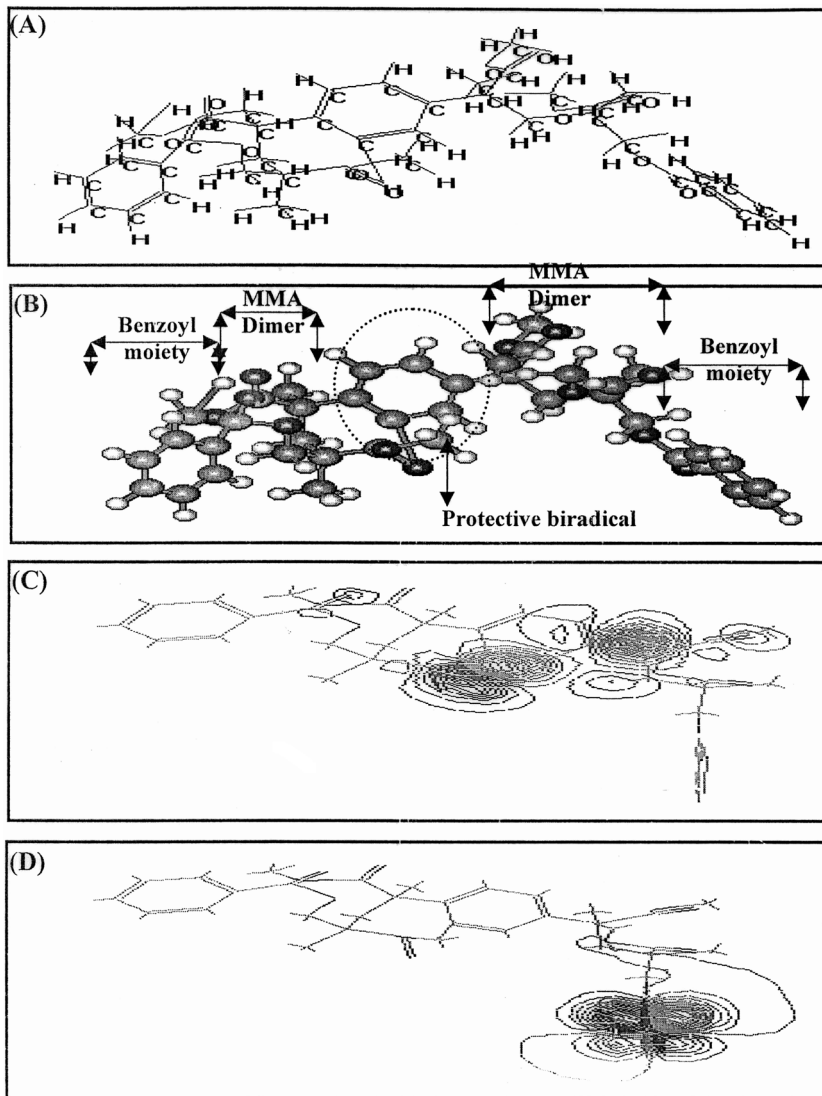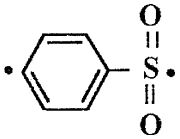
FIGURE 8 Final geometry (A) and (B), (C) HOMO, and (D) LUMO of PMMA protected by phenyl biradical.

4. The comparative studies on the data summarized in Table 4 depend on the iso-structure group pairs, (i.e., carbonyl biradical and thio-carbonyl biradical), and (sulphonyl biradical attached to phenyl ring as benzenesulphonyl biradical or not) and finally phenyl biradicals.
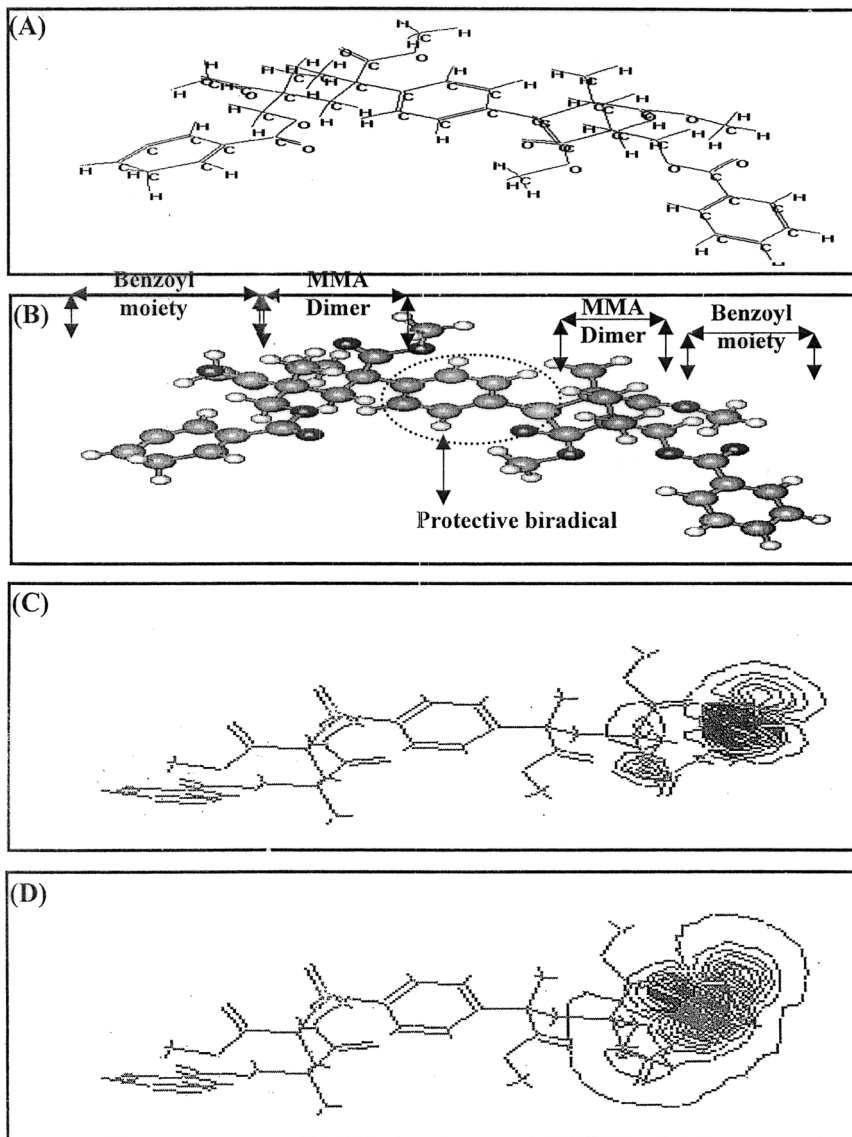
FIGURE 9 Final geometry (A) and (B), (C) HOMO, and (D) LUMO of PMMA protected by benzene sulphonyl biradical.

TABLE 4 Heat of Formation, Total Energy, Energy Gap, and Dipole Moment of Protective Chain of PMMA

Biradical	Heat of formation	Total energy	Energy gap	Dipole moment
S ‖ •C—NH•	−469.7	−9224.6	9.412	5.298
S ‖ •C•	−345.3	−9095.2	7.553	3.148
S ‖ •C—NH•	−420.4	−9319.4	8.064	3.44
O ‖ •S• ‖ O	−475.8	−9610	9.432	4.649
•⬡•	−330.3	−9595.7	8.799	3.841
•⬡—S• (O‖ ‖O)	−8.6	−10413.7	6.897	3.266
O O ‖ ‖ •HN—C—C—NH•	−362.2	−10108.8	9.448	1.735

5. The recombination in the case of carbonyl biradical (c.f. Figure 2) gives ground state energy of −9224.6 eV and heat of formation −469.7 k cal/Mol. The dipole moment computed theoretically is 5.298 D and the energy gap is 9.4 e.V.

6. Replacing carbonyl biradical by (:CS) causes a dramatic change in total energy. The energy of (:CS) is destabilized by ≈129 eV

($\approx$2973 kcal). The dipole moment of (:CS) dropped by 2.15 D. Theoretically, the decrease in dipole moment makes the sulfur protected chain less polar, that is, more stable. This explains why thionyl biradicals [13–14] give efficient protection chains. The obtained data are in good agreement with what was previously found in the literature [15].

7. Replacing carbonyl biradical by biamide biradical (NH−CO−CO−NH) stabilizes the protective chain. The energy of biamide is more stable than carbonyl by 884 eV ($\approx$20332 kcal). The dipole moment of biamide decreases by 0.994 D. Therefore, biamide biradical is more efficient than carbonyl biradical in the protection of PMMA against gamma radiolysis. This is also confirmed by NMR analysis (c.f. Figure 2).

8. Replacing carbonyl biradical (:CO) by sulphonyl biradical stabilizes the protective chain by 386 eV ($\approx$8897 k cal). The dipole moment decreases by 0.66 D. Therefore, sulphonyl biradical is more efficient than carbonyl biradical and thioamide biradical.

9. Replacing carbonyl biradical by phenyl biradical stabilizes the protective chain by 371 eV (8551 k cal) and decreases the polarity of the chain by 1.45 D. Here, again, the phenyl biradical is more efficient in protection than carbonyl, thioamide, and sulphonyl biradicals. This is in good agreement with what was found by molecular weight investigations [16] and NMR spectra (c.f. Figure 2).

10. Replacing phenyl biradicals by benzenesulphonyl biradical stabilizes the protective chain by 818 eV ($\approx$18854 Kcal) and dipole moment decreases by 0.58 D. Therefore, benzene sulphonyl biradical is more efficient than phenyl and sulphonyl biradicals.

CONCLUSION

Polyfunctional ligands (I), (II), and (III) as a source of biradicals to protect the PMMA polymer upon gamma radiolysis are considered theoretically. All the active centers of the studied ligands are π-acceptors and-σ-donors except sulphur atom, which is σ-acceptor. The estimated π-bond order of pairing atoms of ligands (I), (II), and (III) are very small, indicating that these types of bonds are purely single bonds, which under the effect of gamma rays can be easily broken, forming biradicals. The expected biradicals formed after gamma radiolysis for ligand (I), (II), and (III) are given in Table 3.

The recombination process depends on the biradical formed in the reaction medium during gamma radiolysis. The biradicals (A) exist in sufficient amount, and they become more efficient. From the molecular weight measurements during gamma radiolysis, it is observed

that the protective percentage of the prepared ligand has the values of 3%, 7%, and 1% for ligand (I), (II), and (III), respectively [16–20]. On one hand, both ligand I and ligand III have the same sulphonyl biradical and phenyl biradical but in case of ligand (III) a new biradical can be formed (·HN−CO−CO−NH·) and the concentration of phenyl biradical is doubled, the reason for the low protective percent of ligand (III). On the other hand, ligand (II) give the same biradical as ligand (I) and (III), sulphonyl biradical and phenyl biradical, but has two other biradicals (·NH·) and (:CS). The (·NH·) corresponds to (·HN−CO−CO−NH·) in ligand (III) but the difference is in the presence of (:CS) in ligand (II) and phenyl biradical in ligand (III). This means that the phenyl biradical is a more efficient biradical than (:CS), explaining the higher protection percentage in ligand (II).

The structure of the protected chain after recombination of the two polymeric radicals and the biradical produced from the organic ligand are theoretically modeled, because the chains used are asymmetric. Therefore, all interpretation of the ground state properties of the protected chains are qualitative. From the MO-results of the protected chains, it is found that the thionyl, phenyl, and benzenesulphonyl biradicals are more efficient than carbonyl, thioamide, and sulphonyl biradicals, as indicated from the heat of formation, net charges on active centers, charge density, and dipole moments computed theoretically.

This mechanism is also confirmed by the appearance of doublet signals for phenyl protons at $\delta = 7.7$ ppm in case of ligand (I), at $\delta = 7.38$ ppm in case of ligand (II) and at $\delta = 7.3$ ppm in case of ligand (III). Also, the biamide protons appear as two singlet signals at $\delta = 5.6$ ppm and at $\delta = 6.0$ ppm in case of ligand (III). The ^{1}H-NMR spectra are measured after irradiation with 50 kGy and extraction of the additives by solvent extraction and filtration, drying and dissolving in benzene and casting (c.f. Figure 2).

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